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THE

PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS

CONDUCTED WITH THE CO-OPERATION
OF THE
AMERICAN PHYSICAL SOCIETY
BY
EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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THE

PHYSICAL REVIEW.

THE EVOLUTION OF HYDROGEN FROM THE CATHODE AND ITS ABSORPTION BY THE ANODE IN GASES.[1]

By Clarence A. Skinner.

While making an experimental study of the cathode fall of various metals in helium it was observed that no matter how carefully the gas was purified the hydrogen radiation, tested spectroscopically, persistently appeared in the cathode glow. Simultaneous with this appearance there was also a continuous increase in the gas pressure with time of discharge. This change in gas pressure was remarkable because of its being much greater than that which had been observed under the same conditions with either nitrogen, oxygen, or hydrogen.

Now the variation in the cathode fall with current density and with gas pressure in helium was found to be so like that obtained earlier with hydrogen[2] that it appeared necessary to maintain the helium free of the latter in order to make sure that the hydrogen present was not the factor causing this similarity in the results. Futile endeavors to attain this condition led to the present investigation, which locates the *source of the hydrogen in the cathode*, shows that *the quantity of hydrogen evolved* by a fresh cathode *obeys Faraday's law* for electrolytes, and that a fresh *anode absorbs hydrogen according to the same law.*

---

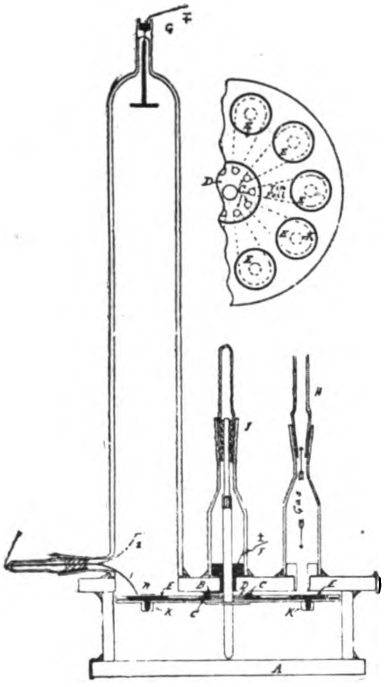
[1] Read in part before the Am. Phys. Soc. at Philadelphia, December, 1904.

[2] Phil. Mag., September, 1904.

PREPARATION AND APPARATUS.

Helium was obtained by heating dry clevite. The gases thus generated stood for some time in tubes containing respectively crushed potassium hydrate and phosphorus pentoxide. From these it was passed into a final purifying chamber consisting of a discharge tube possessing for a cathode an alloy of sodium and potassium, which according to Mey[1] absorbs nitrogen, oxygen, and hydrogen leaving only argon as an impurity in the helium. From this chamber the gas was passed at will into the regular discharge tube containing as electrodes the metals to be tested.

Fig. 1 represents a vertical section of this discharge tube ending below in a larger cylindrical chamber (axis vertical), the whole of glass construction. Ten electrodes *E* (circular disks 15 mm. in diameter) were attached to the face of a circular glass plate at equal intervals by hard rubber caps *K* (see also plan in Fig. 2). This glass plate, mounted in the cylindrical chamber, could be rotated about its axis by the key introduced through the ground joint *J*, and by this means any electrode brought into position at the lower end of the discharge-tube. A hard-rubber disk *D*, studded with brass rivets *C* and fixed to the circular plate, served to complete the electric circuit from *F* through the metal collar and attached spring-brush *B* to the tinfoil strip leading to its corresponding electrode *E*. By this device all electrodes, with the exception of the one in use, were isolated from the circuit. To confine the discharge solely to the face of the electrode, a second circular glass plate properly cut



Figs. 1 and 2.

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[1] K. Mey, Ann. d. Physik (4) 11, p. 127.

was pressed closely on top of the first, covering the tinfoil strips and fitting the rim of the electrodes. Leakage from the brush *B* to the gas was avoided by reducing the space between the upper face of the electrode-plate and the roof of the chamber to about .5 mm. thickness. The discharge-tube was 3 cm. in diameter and about 20 cm. long. All permanent joints of this apparatus which could not be fused were cemented first with water-glass (sodium silicate), then, in addition, they were covered on the outside with de Khotinsky's laboratory cement. The base-plate *A*, which had to be removed to allow for repolishing the electrodes, was sealed by simply applying the latter cement on the outside of the juncture, care being taken that it did not extend to the inner part. This tube proved to be in all cases absolutely airtight.

In connection with this discharge-tube which will be designated as the electrode-tube, was a second Na,K purifying chamber which usually remained in open connection with the electrode-tube so that impurities in the gas filling could be absorbed by simply passing a current from the Na,K as cathode. This allowed also a careful test to be made for any absorption of helium during the operations.

Customary precautions against the presence of moisture were taken. The system on first evacuation remained open to P_2O_5 as dryer at least twenty-four hours, but after that time during all qnantitative tests the drying chamber was cut off by a stop cock. Any moisture appearing, however, would have been wholly removed by the purifying discharge.

Stop cocks and ground joints were lubricated with a mixture of vaseline, rubber and paraffine recommended by Travers[1] as being free of hydrocarbons.

A McLeod gauge served to measure the gas pressure, magnifying it one hundred times.

The electric current was furnished by a battery of small accumulators and measured by a Weston milliammeter.

HYDROGEN IS EVOLVED SOLELY FROM THE CATHODE.

Out of various experiments the following are given as representative of the results obtained.

---

[1] The Experimental Study of Gases.

Helium was prepared and purified and described above. A spectroscopic observation of the discharge in the first Na,K chamber revealed only the lines of helium and argon.

Electrodes of ten different metals having been polished and mounted in the electrode-tube, this with the second Na,K tube and connected chambers was evacuated and left over night open to the P_2O_5 drying chamber. The evacuation was carried the next day to about one thousandth of a millimeter after which the drying chamber with pump was cut off from the rest of the system.

Helium was then admitted to the electrode tube and connecting chambers at a pressure of about three millimeters of mercury. In order to remove the last trace of foreign gases a discharge was passed for some time through the second Na,K tube. The pressure of the gas under this discharge remained unchanged, showing that the spectroscopic test made in the first Na,K tube was reliable.

An electric current of 2 ma. was now passed from one of the electrodos E (Figs. 1 and 2) as cathode and immediately the spectrum of hydrogen appeared in the cathode glow.[1] The gas pressure also increased continuously with the time the current was maintained. After running about three quarters of an hour the rate of evolution of gas became very small. This extra gas evolved (for silver about .2 c.c. at atmospheric pressure) could be absorbed by the Na,K discharge in about an hour.[2] If at the end of this time a current was passed through the tube as before the gas pressure began to increase as at first, but dropped within a very short time to a low rate of evolution. If now at this point a new metal were used as cathode there took place as usual a continuous increase in gas pressure — the rate of evolution of gas being the same for all fresh cathodes. This experiment repeated at various times and with different metals showed beyond doubt that the source of gas was solely in the cathode.

Sixteen different kinds of metals have been tested as cathodes and all except two found to give off hydrogen at a measurable rate. The exceptions were the Na,K alloy which as cathode absorbs hydrogen, and mercury which was distilled in vacuo, then tested without having been in the meantime exposed to the atmosphere.

---

[1] No trace of the hydrogen spectrum appears at any other part of the discharge. The helium radiation itself is obliterated by the argon in the positive column. See Nutting, Bureau of Standards Bulletin, Vol. 1, No. 1.

[2] It was always observed that under this purifying discharge the gas pressure returned to, but never went below, its original value — this showing very definitely that helium did not disappear from the gas filling during any of the operations.

While studying previously the electrode fall in nitrogen, oxygen and hydrogen the gas pressure was found to change very differently with the different gases. Nitrogen increases slowly with the time the current has been passing; oxygen, open to a drying chamber, decreases at a marked rate; while hydrogen was seldom found to change appreciably, though there were occasions where a slight increase was recorded even with hydrogen. If now hydrogen is liberated from the cathode in all gases we should expect in nitrogen an increase in gas pressure arising from the formation of ammonia, which takes place when a discharge passes through a mixture of nitrogen and hydrogen. In this case the rate of increase in gas pressure, compared with that in helium, is small since six atoms of hydrogen would be required to change one molecule of nitrogen into two molecules of ammonia, while in chemically inactive helium one new molecule of gas is formed from two atoms of hydrogen. Likewise with oxygen water vapor would be formed and absorbed by the dryer, in which case four atoms of hydrogen would cause a decrease of one molecule in the gas filling. Of vital interest therefore must be the fact that in hydrogen there is practically no change in the gas pressure when a current passes through it. Experiments described below indicate that in this case the anode absorbs at the same rate as the cathode evolves the hydrogen. Hence we conclude that in all gases hydrogen is evolved from the cathode.

It is rather remarkable that other gases are not present to an appreciable extent. Only in a few cases and that on first usage after polishing has a trace of nitrogen also been observed. Aluminium and tin were noted as giving off a trace of nitrogen.

THE METAL RECOVERS A SUPPLY OF HYDROGEN BY DIFFUSION FROM WITHIN.

An endeavor was made to deplete the metals of their supply of hydrogen by passing from them as cathode a current for a sufficient length of time, but it was soon found that they recovered more or less rapidly from their apparently depleted condition. Silver which exhibits this property of recovery to a high degree happened to be the first metal tried and it was so persistent in regaining its original store that other metals have received comparatively slight attention though all have been observed to possess within themselves the property of recovering to a certain degree their ability to give off hydrogen.

With a freshly polished metal as cathode the gas pressure increases at first at a constant rate, but after a time this rate begins to drop off until the pressure appears to have reached a constant maximum value. Silver was depleted in this way giving off about two tenths of a cubic centimeter (measured at atmospheric pressure) of hydrogen. The current was then broken and the hydrogen absorbed by the Na,K cathode. After standing in the helium over night then tested again the next morning it was found to have a new supply equal to the one given up the day before. Without allowing it any chance of regaining hydrogen from an external source it was thus depleted six or eight times during the course of two weeks and found to give off at each time about the same amount of gas. With an hour's rest only a slight recovery was noticed.[1]

After this series the silver was removed from the tube, repolished, then tested again with the same results. Altogether about two cubic centimeters of gas have been given off by this silver disk, which is 15 mm. in diameter and about one millimeter thick. It shows no sign of having its supply of hydrogen reduced in the least. There are other metals of which cadmium is an example which seem to possess more of a surface charge of hydrogen. This metal, however, seems to reach an apparently depleted condition before the hydrogen it really possesses (measured by vaporizing the surface) is half gone.[2]

---

[1] H. A. Wilson has observed a similar recovery in case of the escape of negative electricity from hot platinum. Phil. Trans., 202, p. 243, 1903.

[2] A single experiment was performed in which the surface of a cadmium cathode was vaporized by an extra large current. The cathode gave off about one third of a cubic centimeter of gas with the first vaporization. With a second an inappreciable quantity was freed as if its supply had been exhausted.

Just what takes place, therefore, causing the metal to appear depleted is not clear. Undoubtedly the tarnish which appears on the surface of all metals as cathode plays a part in decreasing the diffusion of hydrogen outward from metal into gas. It is natural to suppose that with this present, the hydrogen after discharging to the positive gas ion which has penetrated this film, diffuses more readily back into the metal than outward through the film. Thus it has been noted that those metals, like silver, which tend to keep clean by the process of dusting off onto surrounding bodies will completely recover with rest, while aluminium for example, which under first usage gives off hydrogen with remarkable freedom, but which does not dust off appreciably, recovers but slightly after its surface becomes once tarnished.

All metals are renewed by being repolished, but whether this arises wholly from cleaning the surface of the metal or partly also from exposure to the moist atmosphere remains undecided. The kind of polish used does not seem to affect the results.

This question of depletion is considered again in connection with the experiments on steel cathodes differing greatly in discharge area.

TESTED AT LOW PRESSURES THE METALS DO NOT ABSORB HYDROGEN IN THE MOLECULAR STATE.

It is of first importance to know under what conditions the metals gain their store of hydrogen. The metallurgical processes may account for it in many cases but it is questionable if all metals would retain the gas to such a concentration through the processes of fusion to which they are subjected.

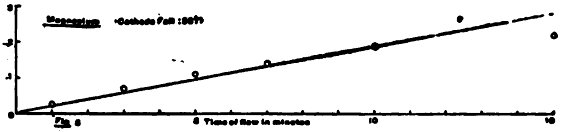
Platinum is a well-known representative of metals which, with evolution of heat, absorb hydrogen in large quantities — giving it up again as the temperature is raised. Now it may be possible that the other metals also absorb hydrogen in relatively smaller quantities. The apparatus as it stood allowed a delicate test to be made at low gas pressures. Hydrogen was driven out of the different metals in the electrode tube to a pressure of about one half millimeter in three millimeters of helium. This was left standing in the tube over night. The next day the gas pressure was found unchanged. The quantity of hydrogen reabsorbed by the metals was less than one twentieth part of the amount the silver alone recovered in that time. This experiment shows that the hydrogen in the molecular state is not at such low pressures absorbed by the metals. It is, however, by no means conclusive, for, from a thermodynamic standpoint we should expect absorption to take place with the pressure sufficiently great.

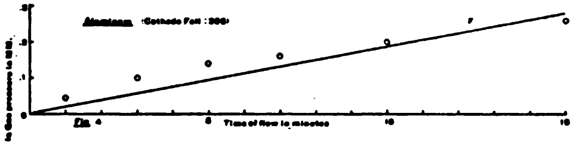
The indications are that in the metal the hydrogen exists in the atomic state rather than in the molecular. It is probable, therefore, that hydrogen in the atomic state would be readily absorbed by the metals while no appreciable amount is taken up if the gas be in the molecular state. Some metals, such as platinum and palladium, appear able to dissociate and absorb large quantities of hydrogen. Any dissociating agent such as water might, therefore, render hydrogen in a form readily absorbed by all metals.

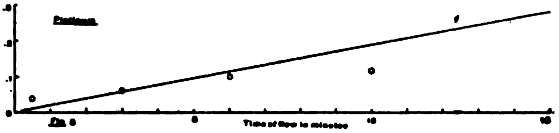
THE QUANTITY OF HYDROGEN EVOLVED FROM THE CATHODE OBEYS FARADAY'S LAW.

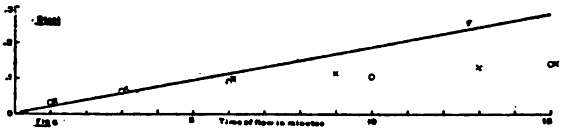
Measurements were made of the rate of evolution of hydrogen from cathodes of various metals. This was obtained by first determining the space occupied by the gas (620 c.c.) and then from the increase in gas pressure calculating the quantity of hydrogen given off. Ten electrodes could be tested without opening the tube or even changing the gas filling. The metals were freshly polished and introduced into the tube which was immediately evacuated and left standing open to the drying chamber over night. The next day after continued evacuation the drying chamber and pump were cut off and helium admitted at the desired pressure. Before passing a current through the electrode tube a purifying discharge was passed through the Na,K tube to assure the removal of any trace of foreign gases. After testing one metal the gas evolved was absorbed by the purifying discharge, then another metal immediately tested. With the exception, therefore, of the lapse of time all metals were tested under identical conditions.

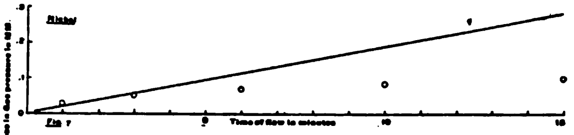
Results with a current of 2 ma. in helium at 3 mm. pressure are represented by points in Figs. 3–14, in which the ordinate of each point represents the increase in gas pressure while the corresponding abscissa represents the time the current had been flowing. The diagonal line *F* in each figure shows the calculated increase in gas

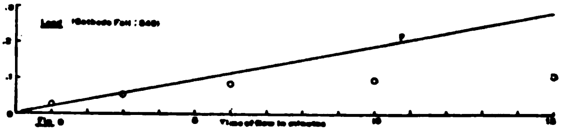

Magnesium (Cathode Fall : 387)
.3
.2
.1
0
Fig. 3
5 Time of flow in minutes
10
15

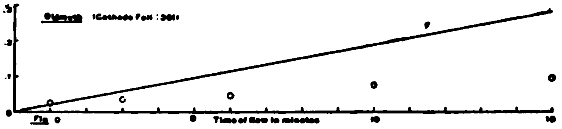

Increase in Gas pressure in mm.
Aluminium (Cathode Fall : 366)
.3
.2
.1
0
Fig. 4
5 Time of flow in minutes
10
15

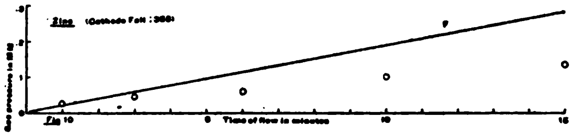

Platinum
.3
.2
.1
0
Fig. 5
5
Time of flow in minutes
10
15

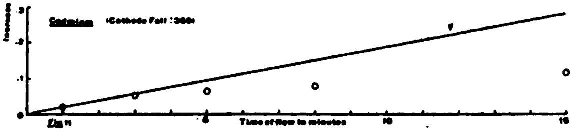

Steel
.3
.2
.1
0
Fig. 6
5
Time of flow in minutes
10
15

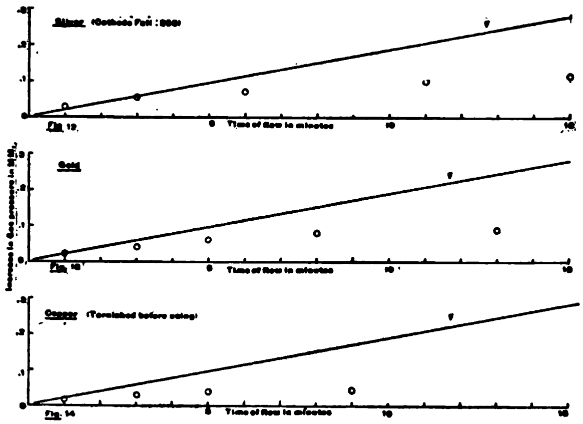

Increase in Gas pressure in mm.
Nickel
.3
.2
.1
0
Fig. 7
5
Time of flow in minutes
10
15


Lead (Cathode Fall : 346)
.3
.2
.1
0
Fig. 8
5
Time of flow in minutes
10
15


Bismuth (Cathode Fall : 361)
.3
.2
.1
0
Fig. 9
5
Time of flow in minutes
10
15


Increase in Gas pressure in mm.
Zinc (Cathode Fall : 368)
.3
.2
.1
0
Fig. 10
5
Time of flow in minutes
10
15


Cadmium (Cathode Fall : 368)
.3
.2
.1
0
Fig. 11
5
Time of flow in minutes
10
15



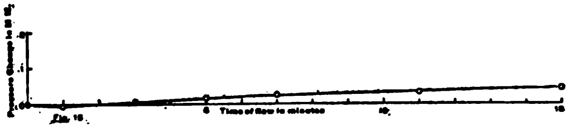
pressure if Faraday's law for electrolytes should govern the evolution. All metals show that the hydrogen is liberated for a time at a rate sufficient to carry, as negatively charged atoms, the whole current between cathode and gas. After a lapse of time, varying in magnitude with the kind of metal used, the rate of evolution drops below that required by Faraday's law. The tendency is general for the metals to give off in the first minute a quantity greater than that necessary. This extra pressure does not arise from heating nor from dissociation of the gas under the current, for these effects were found too small to be observable. It is probable that the current on "making" the circuit is extra large, but of such short duration as not to be revealed by the ammeter. Experiments with hydrogen described below show that it cannot arise from *neutral* gases freed from the electrode and chamber walls.

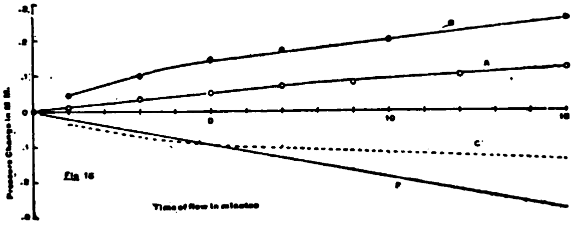
Other tests made with helium, down to a pressure of one millimeter, and also with currents varying from one to three milliamperes corroborated this law, though experimental conditions were not so favorable for making reliable measurements. For with larger currents pressure observations could not be read rapidly enough, and at lower gas pressures the Na,K cathode does not absorb the last trace of hydrogen so that the assurance was lacking that a disturbing quantity of hydrogen was not already present. The experiments were extended, however, to test the effect of a greatly varied current density at the cathode. The current density in the experiments described above was about six times the normal, or minimum, value for helium at that pressure. Another experiment was performed using a steel wire (diam. 3 mm.) as cathode. With a current of 2 ma. and pressure of helium 3 mm. the normal discharge area was 10 sq. cm. The pressure change with this cathode is given by the crosses in Fig. 6; while that observed with a steel disk (discharge area, 1.7 sq. cm.) is represented by circles. The two sets of results are practically identical over the whole range. Evidently the deviation from Faraday's law, being the same with both cathodes, cannot be ascribed simply to exhaustion of the store of hydrogen, for in that case the wire should have kept up about six times as long as the disk. If, on the other hand, it be ascribed to tarnish alone, this must take place at a rate which is the same for greatly different current densities. Another possible factor is the absorption of hydrogen by the anode, but since the quantity here makes up less than one per cent. of the gas filling anode absorption could not be expected to play an appreciable part. The difference in results from the different metals also precludes this as a possible explanation.

A comparison of the length of time the different metals follow Faraday's law in furnishing hydrogen brings to light an interesting relation between this and their cathode fall when fresh. It is a well-known fact that aluminium and magnesium possess in all gases a lower cathode fall than the rest of the more electronegative metals. In several of the foregoing figures is given the cathode fall (obtained during another series of experiments) of the fresh metal in helium under a current of 0.6 ma. and gas pressure of 2 mm. With the difference in cathode fall aluminium and magnesium are to be distinguished from the other metals in a more striking manner by the freedom with which they continue to give off hydrogen. These results suggest that there must be an intimate connection between the cathode fall of the fresh metal and the length of time the metal holds up in furnishing hydrogen. Though the quantity of hydrogen possessed by such metals as platinum and silver is much greater than that possessed by aluminium and magnesium, we find the latter give off during a fifteen-minute run about twice as much as the former, indicating that the cathode fall must be affected to no small extent by the rate with which the hydrogen diffuses through the metal.

In Hydrogen the Anode Absorbs at the Same Rate the Cathode Evolves It.

Reference has already been made to the fact that earlier observations with a hydrogen filling show only occasionally a slight increase in gas pressure. Thinking it probable that we have in this case to do with absorption by the anode neutralizing the evolution from the cathode a test was made to see what takes place under a longer run than was made in earlier experiments. With the silver disk as anode and an aluminium wire, of about half the discharge area of the silver, as cathode, a current (2 m.a.) was passed through hydrogen at pressure 3.45 mm. and pressure measurements made at definite intervals. The observed change is represented by the curve in Fig. 15. During the first three minutes of discharge the gas pressure remained practically unchanged, but at the end of that time it began to increase at a measurable rate. The most natural explanation of these results seems to be that of anode absorption. At first the anode absorbs all negative atoms discharging to it. These do not diffuse into the metal as rapidly as they are given off by the cathode, therefore the concentration in the anode surface increases up to a point where uncharged atoms diffuse out again into the gas. Beyond this point the curve would therefore represent the difference between the rate of diffusion out of the cathode and that into the anode.





If this be the correct explanation the effect should be magnified by taking an anode of much smaller discharge area than the cathode possesses. This experiment was tried. The cathode was the disk of aluminium used in the experiments described above. For anode an aluminium wire sheathed with glass tubing was used giving a discharge area something less than one tenth that of the cathode. Observations were made in hydrogen as before (current 2 ma., gas pressure 3 mm.). The results given in Fig. 16, curve *A*, substantiate the supposition just expressed. The pressure begins to increase before the discharge has continued one minute. The form of the curve is that which might be expected as a difference between cathode evolution and anode absorption. Assuming that the cathode gives off hydrogen at the same rate here as in helium (represented by curve *B*) the curve *C*, representing anode absorption is obtained as the difference between the *A* and *B* curves, the anode absorption tending to reduce the gas pressure by the amount indicated. The general form of this curve appears to be the same as that given by cathode evolution in helium. Here the line *F* represents absorption demanded by Faraday's law. These experiments indicate therefore that *in hydrogen a fresh anode absorbs gas at a rate also determined by Faraday's law.*

DISCUSSION.

Some interesting conclusions, drawn from the experimental results recounted on the preceding pages, may be stated briefly.

With fresh electrodes the hydrogen atom serves in all gases as carrier of the electric current from cathode to gas. With a gas filling of hydrogen the atom serves also as carrier from the gas to the anode — by which it is absorbed. In helium on the other hand the hydrogen atom leaving the cathode discharges to the helium and this transmits the current to the anode, the negative helium ion discharging without being absorbed.

Most remarkable of all is the fact that, though there is a considerable concentration of *free positive ions* at the cathode surface, *they do not discharge to the metal* so long as it furnishes hydrogen sufficient to carry the current. This condition may last several minutes. Even the positive hydrogen ion does not enter into electrical union with the metal, though a negatively charged hydrogen atom is readily absorbed by it.

The generally accepted view that the negative ion in gases is of smaller magnitude than an atom while the positive ion is of molecular (or atomic) magnitude evidently does not hold there. We have strong evidence in the above experiments that in hydrogen a hydrogen atom carries the current from cathode to the gas, then again from the gas to the anode. This being true any other form of ionization in the gas between cannot be expected. If now this occur with hydrogen we should expect no other than atomic ions under the same conditions in other gases. Conduction in other gases would however be modified by the fact that the negative hydrogen atom freed from the cathode serves as the active ionizing agent. This fulfills in all gases except hydrogen the requirement that the negative ion be much smaller than the positive ions it produces. Of special interest in this connection are the results recently published by Townsend.[1] He finds that the positive hydrogen ion possesses an unexpectedly large ionizing power, which seems to agree with the views just presented requiring that the only difference between the ionizing power of the negative ions freed from metals (negative hydrogen atoms) and positive ions produced in hydrogen (positive hydrogen atoms) be that arising from the difference in sign of the charge carried.

The effect of an electric current and radiations in producing chemical combination of gas mixtures receives on this basis a simple explanation. The gas molecules are broken up into their constituent atoms and these recombine, forming the new compound.

Some light also is thrown by these experiments on the problem as to why positive gas ions do not discharge to a negative metal but instead draw out of the metal the negative hydrogen ions. It appears that an intimate association in the atomic form is necessary to a transmission of charge from gas to metal. Now hydrogen in acids is universally the carrier of positive electricity. In solutions of metallic salts the metals carry universally the positive charge. Here, however, when we have an electrical union of hydrogen with the metals, the hydrogen becomes the carrier of the negative charge. The natural union therefore of all gases with metals should be that where the metallic atom is positively charged and the gaseous atom negatively charged. If this be reversed — the metal being charged with negative electricity and the gas with positive — a union only takes place under very great external forces. For as the cathode becomes depleted the electric force at the boundary between it and the gas is increased greatly. This conclusion is derived from observations made on the cathode fall in nitrogen. About three years ago[1] the writer observed with a steel cathode in nitrogen that there was at first, as usually observed, a strong electric field out in the gas between the cathode and the inner boundary of the negative glow. After, however, a sufficiently large current was passed for a few moments this field dropped to practically zero. At the same time, however, the fall of potential between the cathode and the negative glow increased, which shows that there must have taken place a considerable increase in the electric force at the boundary between metal and gas. This change is now recognized as that where the hydrogen ceased to be furnished by the cathode as required by Faraday's law. It may be possible that this represents the force required to cause the positive ions of the gas to discharge to the metal at the rate demanded by the current. It may be that such an electrical union is wholly impossible, and cathode rays a result. A most interesting experiment in this connection would be one to determine what effect, if any, the hydrogen atoms emanating from the cathode produce on the intensity of cathode rays. The writer hopes to make some experiments bearing on this in the near future.

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[1] Phil. Mag., December, 1904.

PHYSICAL LABORATORY,
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[1] Phil. Mag. (6), 2, p. 616, 1901.

APPLICATION OF THE HYPOTHESIS OF DISSOLVED ICE TO THE FREEZING OF WATER AND OF DILUTE SOLUTIONS.

BY C. S. HUDSON.

PURPOSE AND INTRODUCTION.

THE belief is becoming general that water is not composed of molecules of the same kind, but rather that molecules of dissolved ice are present in the liquid. The principal evidence for this assumption is the fact that most of the abnormal properties of water, such as its temperatures of maximum density and of minimum compressibility, the increase of its coefficient of thermal expansion with increasing pressure, and its decrease of viscosity under pressure, can be readily explained by the hypothesis that a portion of the water has the same properties that would be ascribed to dissolved ice if the aqueous solution of dissolved ice be analogous to the solutions of most non-electrolytes.[1] It is the purpose of this article to investigate further by means of the methods of thermodynamics this question of dissolved ice, and it may be mentioned in advance that the chief conclusion here obtained is the proof that if we ascribe to the dissolved ice a definite solubility, together with a definite *equilibrium-concentration*, it is possible to account for the constant freezing temperature of pure water and also for the lower freezing points and temperatures of maximum density of dilute aqueous solutions. The first of these results is a matter of rather common knowledge among chemists and physicists,[2] but the other two conclusions are new and constitute further evidence for the hypothesis of dissolved ice.

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[1] Röntgen, Ann. d. Physik., 45, 91–97, 1892; Sutherland, Phil. Mag., 50, 460–489, 1900.

[2] Cf. Bancroft, Journ. Phys. Chem., 2, 143, 1898; Roozeboom, Zeitschr. physik. Chem., 28, 289, 1899.

Whether the dissolved ice-molecules that are supposed present in water are identical with the associated molecules of water is unknown and is not essential to the following thermodynamical study. Without making any restriction concerning the formula of the dissolved ice, we will assume that it has the property common to all crystalline solids of crystallizing from solution when the necessary conditions of supersaturation are fulfilled, or in other words that the dissolved ice has a definite solubility which is, like all solubilities, variable with the temperature. Furthermore, if the presence of such a substance dissolved in water and producible from it be assumed, it follows that a state of equilibrium exists between the dissolved ice-molecules and the solvent water-molecules which can be expressed by the equation

$$\underset{\text{(dissolved ice)}}{m(\mathrm{H_2O})_n} \rightleftarrows \underset{\substack{\text{(solvent water-}\\ \text{molecules)}}}{n(\mathrm{H_2O})_m} \qquad (A)$$

where n and m are integers expressing the degree of polymerization of the two substances in terms of the molecule of water-vapor as unit. The state of equilibrium represented by this equation is variable with the temperature and at a given temperature there is a concentration of dissolved ice, here called the *equilibrium-concentration*, which is in equilibrium with unit concentration of solvent water-molecules. At constant temperature and pressure this equilibrium-concentration is invariable for pure water, and an attempt to alter it by direct addition or withdrawal of either of the constituent substances must prove futile, because the system is not composed of two independent components. If these two concentrations of dissolved ice, namely the solubility and the equilibrium-concentration, be assumed, and the laws of dilute solutions be applied to water, a number of results follow, which will be given under the following six headings: (1) The relation of the solubility and equilibrium-concentration curves to the freezing-temperature of pure water, (2) the necessity of a constant freezing-temperature of water, (3) the maximum work obtainable by the freezing of ice from pure water and from a dilute solution, (4) the lower freezing-temperatures of dilute solutions, (5) calculation of the molecular depression of the freezing point by aid of the foregoing hypothesis, (6) the lower temperatures of maximum density of dilute solutions.

1. THE RELATION OF THE SOLUBILITY AND EQUILIBRIUM-CONCENTRATION CURVES TO THE FREEZING-TEMPERATURE OF PURE WATER.

Let the solubility of the dissolved ice in unit concentration of the solvent water-molecules at any given temperature be S, and the equilibrium-concentration at the same temperature be C_w. At temperatures where S is greater than C_w, the dissolved ice does not saturate the solvent, there is no tendency for ice to precipitate, and consequently water is stable at these temperatures. Such temperatures are obviously above the freezing temperature. On the other hand, at temperatures where C_w is greater than S, there is more ice in solution than corresponds to its solubility and this excess can precipitate, the water can freeze. At such temperatures, which are obviously below the freezing-temperature, water can be considered to be a supersaturated solution of ice. It is plain that at the freezing-temperature $C_w = S$. These relations are illustrated by the accompanying diagram, in which the coördinate axes measure temperature and concentration of dissolved ice respectively. The intersection of the curve of solubility, S, with that of equilibrium concentration, C_w, gives the freezing temperature of pure water under ordinary atmospheric pressure. If the pressure be introduced as a third variable and be measured along a third axis perpendicular to the plane of the paper, the S and C_w lines become surfaces and the freezing-temperatures for the various pressures lie on the line of intersection of these two surfaces. How these surfaces change with the pressure is not known, but their intersection, the line of freezing-temperatures, approaches the concentration-axis with increasing pressure, because the freezing-temperature is known to be lowered by pressure.

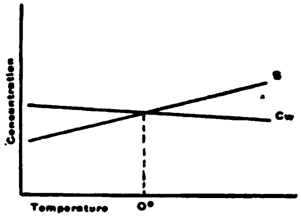

Fig. 1.

2. THE NECESSITY OF A CONSTANT FREEZING-TEMPERATURE.

If an isolated system composed of undercooled water be imagined and the precipitation of some of the excess of dissolved ice be considered begun, the accompanying evolution of heat will raise the temperature of the system and thus cause the equilibrium-concentration to approach the solubility (compare Fig. 1). Since the process of precipitation causes the rise of temperature, it is evident that the temperature will not rise appreciably beyond a point at which the precipitation ceases, provided the establishment of the new equilibrium-concentration that follows a change of temperature takes place with great rapidity. This limit beyond which the temperature of the freezing water cannot rise is obviously the temperature at which the equilibrium-concentration is equal to the solubility, namely, 0°. That the system will continue to rise toward this limiting temperature so long as undercooled water is present is evident from the relations of Fig. 1, because as long as water below 0° is present in contact with solid ice, the supersaturated solution will precipitate ice and an accompaning rise in temperature will occur.

3. THE MAXIMUM WORK OBTAINABLE BY THE FREEZING OF ICE FROM PURE WATER AND FROM A DILUTE SOLUTION.

The formation of ice from water can take place in at least three ways, namely, by distillation, by the freezing of pure water, and by the freezing of a solution. The details of each of these processes will now be considered, the aim being to calculate the maximum work obtainable from the freezing.

A. *Formation of Ice by Isothermal Distillation.* — At the temperature T let the vapor pressure of pure water be P_w and that of ice P_i. Consider the following isothermal and reversible process. n mols (n 18 gr.) of the undercooled water are evaporated at the constant vapor-pressure P_w; the resulting gas is expanded from P_w to P_i, and then condensed to ice. The total work obtainable from the system during the formation of one mol of the ice is

$$W = nRT + nRT \log \frac{P_w}{P_i} - nRT = nRT \log \frac{P_w}{P_i}. \qquad (1)$$

Since the indicated isothermal process is reversible, the work W is the maximum work or free energy of the change.

B. *Formation of Ice by Freezing Pure Water.* — Consider at temperature T a mass of water in equilibrium which contains C_w mols of ice (nC_w 18 gr.) dissolved in one mol of the solvent water-molecules. By means of an osmotic wall operating so rapidly that no chemical reaction as indicated by equation (A), page 17, takes place during the following physical changes, concentrate the dissolved ice from C_w to S, the solubility of the ice at the temperature T, and then press out the dissolved ice at constant concentration S to form solid ice; the maximum amounts of work obtainable from the system during these two changes are, respectively,

$$W_1 = C_w RT \log \frac{C_w}{S} \text{ and } W_2 = - C_w RT.$$

Although the indicated procedure causes the formation of C_w mols of solid ice, it is to be noticed that the resulting system is not composed of ice and ordinary water, because the original water has been deprived of its dissolved ice and has therefore become unstable. In order to calculate the maximum work that is to be obtained from the changing of this unstable water to the stable form, we proceed as follows: Since the unstable water does not contain the dissolved ice, its vapor-pressure P_u would be expected to be greater than that of the stable water, and would be given by the formula of Raoult,

$$\log \frac{P_u}{P_w} = C_w, \text{ or } \log P_u = \log P_w + C_w.$$

If the mol of unstable water which was produced in forming the ice be evaporated at its vapor-pressure P_u, and the resulting gas be then changed in concentration from P_u to P_w and condensed to form stable water, the desired condition of equilibrium is reached in a reversible manner and the work obtained from the transformation of the unstable water to the stable form is

$$W_3 = RT + RT \log \frac{P_u}{P_w} - RT = RT \log \frac{P_u}{P_w}.$$

If the value of log P_u that was given above be substituted in the last equation, it is found that $W_3 = C_w RT$. The total work to be obtained from the freezing of stable water to form C_w mols of ice is

$$W_1 + W_2 + W_3 = C_w RT \log \frac{C_w}{S},$$

and the maximum work per mol of ice formed is

$$W = RT \log \frac{C_w}{S}. \qquad (2)$$

C. *Formation of Ice by Freezing a Dilute Solution.* — Imagine at constant temperature T a reservoir made up in the following manner. A dilute aqueous solution is to be in contact with a non-miscible liquid, which shall have the property of dissolving the ice-molecules readily, but not the water-molecules.

Let the vapor pressure of the aqueous solution be P_s and the concentration of the ice in it be C_s; then if the solubility of the ice be S' in the second solvent and S in water, the concentration of ice in the second solvent when the reservoir can be in equilibrium will be $C_s\, S'/S$. By means of an osmotic wall operating so rapidly that no chemical reaction as given by equation (A), page 17, takes place in the second solvent, draw out from the aqueous solution into the second solvent one mol of dissolved ice at the constant concentration $C_s\, S'/S$, whereby the work RT is obtained from the system. In order to keep the reservoir in equilibrium during this change, n mols of water are distilled into the aqueous solution while the ice is being drawn out, and by this distillation the work

$$nRT \log \frac{P_w}{P_s}$$

is obtained. At this stage, contact between the two liquids is to be broken and the mol of ice is to be compressed from concentration $C_s\, S'/S$ to S' and then pressed out of solution at constant concentration S'. During the last two changes the work

$$RT \log \frac{C_s \frac{S'}{S}}{S'} - RT = RT \log \frac{C_s}{S} - RT$$

is produced, and the total work to be obtained from the freezing of one mol of ice in this isothermal and reversible manner is

$$W = RT \log \frac{C_s}{S} + nRT \log \frac{P_w}{P_s}. \qquad (3)$$

4. THE LOWER FREEZING-TEMPERATURES OF DILUTE SOLUTIONS.

If the expressions (1), (2) and (3) of the preceding section for the free energy of the freezing of water to form one mol of ice be placed equal to one another, the following relations are obtained:

$$\frac{C_w}{S} = \left(\frac{P_w}{P_i}\right)^n, \tag{4}$$

$$\frac{C_s}{S} = \left(\frac{P_s}{P_i}\right)^n, \tag{5}$$

$$\frac{C_w}{C_s} = \left(\frac{P_w}{P_s}\right)^n, \tag{6}$$

From the last equation it is evident that the equilibrium-concentration for a dilute solution is less than that for pure water at the same temperature, because the vapor-pressure of the solution is less than that of pure water. This conclusion that a dilute solution contains less dissolved ice than does pure water, has an important consequence; for it is therefore evident that a dilute solution can not precipitate ice at the freezing-temperature of water, but must be cooled to a lower temperature in order to cause the concentration of ice in the dilute solution to become equal to the solubility of ice in water.[1] The accompanying figure illustrates the relations which are under consideration. The coördinate axes and the curves S and C_w have the same significance as in Fig. 1, and the curve C_s represents the equilibrium-concentrations for a dilute solution. The intersection of S with C_w represents, as before, the freezing-temperature of pure water, and the intersection of S with C_s gives the lower freezing-temperature of the dilute solution.

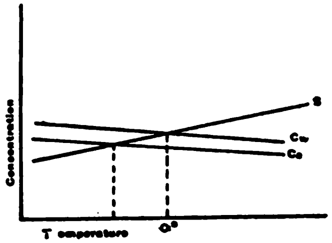

Fig. 2.

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[1] It is assumed in drawing this consequence that the solubility of ice in the dilute solution is not appreciably different from its solubility in water.

5. CALCULATION OF THE MOLECULAR DEPRESSION OF THE FREEZING TEMPERATURE FROM THE FOREGOING HYPOTHESIS.

Consider a solution containing a mols of foreign substance dissolved in 1,000 grams of water, and let its freezing-temperature be $(273 - dT)$. If $C_{s,\,dT}$ and S_{dT} represent the equilibrium-concentration and solubility respectively for the solution at its freezing-temperature, the equality $C_{s,\,dT} = S_{dT}$ holds. If H_s denotes the heat of solution of ice per gram,

$$\log S_{dT} - \log S_0 = + \left(\frac{H_s n \cdot 18}{RT^2}\right) dT,$$

in which S_0 denotes the solubility of ice at zero degrees. This equation can be rearranged to

$$\log S_{dT} = \log S_0 + \frac{H_s n \cdot 18}{RT^2} dT. \tag{7}$$

Equation (6), page 22, gives the relation

$$n \cdot \log \frac{P_{w,\,dT}}{P_{s,\,dT.}} = \log \frac{C_{w,\,dT}}{C_{s,\,dT}},$$

and since the law of Raoult gives

$$\log \frac{P_{w,\,dT}}{P_{s,\,dT}} = \frac{a \cdot 18}{1{,}000},$$

it follows that

$$\log C_{s,\,dT} = \log C_{w,\,dT} - n \frac{a \cdot 18}{1{,}000}. \tag{8}$$

Now if H_T denotes the heat of formation of one gram of the dissolved ice, we have an equation similar to the second one in this section, or,

$$\log C_{w,\,dT} = \log C_{w,\,0} + \frac{H_T n \cdot 18}{RT^2} dT.$$

If this value of $\log C_{w,\,dT}$ be substituted in equation (8), and the resulting value of $\log C_{s,\,dT}$ be placed equal to (7), it follows, since $C_{w,0} = S_0$, that

$$dT = \frac{a \cdot 18}{1{,}000} \cdot \frac{RT^2}{18(H_T - H_S)}.$$

Now the expression $(H_T - H_S)$ is equal to the heat of fusion of one gram of ice, *i, e.*, L calories, or,

$$dT = \frac{a}{1{,}000} \cdot \frac{RT^2}{L}.$$

6. The Lower Temperatures of Maximum Density of Dilute Solutions.

It was first clearly explained by Röntgen (*loc. cit.*) that the occurrence of the temperature of maximum density of water may possibly be due to facts connected with the presence of ice dissolved in the water. According to this view a rise in temperature would cause water to change in volume as the result of the effect of heat both upon the volume of the solvent water-molecules and upon the equilibrium-concentration. The former of these effects is supposed to be an increase of volume with increasing temperature, and the latter, a decrease in equilibrium-concentration and consequently in volume with increasing temperature; and it is obviously possible that these two opposing changes of volume may just neutralize each other at the temperature of maximum density. Röntgen has also shown that the lowering of the temperature of maximum density by increased pressure is a fact in agreement with this view of the cause of the temperature of maximum density; for it would be supposed that the equilibrium-concentration would be diminished by subjecting the water to increased pressure, and therefore the change of volume that is due to the effect of temperature upon the equilibrium-concentration would be correspondingly decreased.

I wish to add to this argument that the fact that solutions have temperatures of maximum density lower than that of pure water is also in complete agreement with the hypothesis of dissolved ice; for if we accept the conclusion of section four that solutions contain less dissolved ice than does pure water, the reasoning of the previous paragraph concerning the change of maximum density with pressure applies also to the influence of dissolved substances upon this temperature. In this connection it is to be emphasized, however, that the temperature of maximum density of a solution cannot be expected to be subject to such simple conditions as is the freezing-temperature of the solution, because the effect of temperature upon the volume of the dissolved substance, which is a specific property of the solution, must certainly be an important factor in determining the temperature of maximum density. It is even possible that this specific influence of the solute may be great enough in exceptional cases to cause the temperature of maximum density to increase with the concentration of the solution. On the other hand, it can be expected that the majority of dissolved substances will lower the temperature of maximum density, and that equimolal solutions of substances which possess similar chemical and physical properties will have the same temperature of maximum density. This expectation agrees strikingly with the recent measurements of Müller,[1] who found that the lowering of the temperature of maximum density caused by dissolving various organic compounds in water is proportional to the concentration of the solution and has the following values for molal solutions of the different substances, which are here grouped in accordance with their constitutional similarity.

	°
Phenol	7.2
Pyrocatechin	7.7
Hydroquinone	7.4
Resorcin	7.6
Pyrogallol	8.7
Phloroglucin	7.8
Mannite	11.1
Dextrose	10.1
Oxalic acid	12.2
Succinic acid	12.5
Tartaric acid	15.7

It is obvious that equimolal solutions of substances of similar composition have very nearly the same temperatures of maximum density.

SUMMARY.

The contents of this article may be summarized as follows:

Following the hypothesis advanced by Röntgen in 1890, it has been shown that if cold water contains ice dissolved in it, it is probable that the ice has a definite solubility in the water, and also a definite *equilibrium-concentration*, both of these concentrations varying with the temperature independently.

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[1] Zeitschr. physik. Chem., 43, 109–114, 1903.

The assumption of the existence of these two concentrations will account for the constant freezing-temperature of pure water, and this temperature has been shown to be the temperature at which the *equilibrium-concentration* is equal to the solubility.

Three values for the free energy of the freezing of water have been derived, corresponding to the three methods by which the water was frozen, namely, by distillation, by freezing pure water with the aid of an osmotic wall, and by freezing a dilute solution. From the equality of the values of these expressions of the free energy of freezing, it follows that the concentration of ice in a dilute solution is less than the concentration of ice in pure water at the same temperature. It has then been shown how this conclusion will account for the fact that dilute solutions have lower freezing points and lower temperatures of maximum density than pure water, and the formula for the molecular depression of the freezing temperature, $dT = \frac{a}{1,000} \cdot \frac{RT^2}{L}$, has been derived from the foregoing hypothesis that water contains ice dissolved in it.

Physical Laboratory, Princeton University,
January, 1905.

COLOR IN PLATINUM FILMS.

By Isabelle Stone.

WHILE making platinum films by cathode discharge I found that, using a platinum point as cathode, I obtained colored rings on a glass plate placed directly under the point. In order to investigate this phenomenon, I got together the necessary parts for a receiver of the kind shown in the diagram. The receiver *A* fitted into a circular groove cut out of the aluminum plate *xy*. This aluminum plate contained a binding post *B*, and inside the receiver, two aluminum supports *K* and *L* on which the glass plate *J* rested. Through the neck of the receiver fitted a hollow ground-glass stopper *C*. *C* was in connection with two branch tubes *D* and *E* in each of which fitted ground-glass stopcocks *F* and *G*. Through the top of the ground-glass stopper *C* was fused a loop of platinum wire ending within the receiver in a hook. To the outer loop *H* the wire from the secondary coil was attached. To the inner hook any form of cathode could be suspended. The cathode first used was a thick platinum wire sealed into a glass tube with enough of the wire left at the upper end to form a loop for suspension and two millimeters left at the lower end to form the cathode. The stopcock *G* was turned to shut off the entrance of air and the tube *E* being joined through a drying tube to a pulsometer oil pump, stopcock *F* was left open and the exhaustion of air from the receiver commenced. Later, when it became necessary to measure accurately the pressure of the air in the receiver, the tube *D* was connected to a McLeod gauge by means of the two-way stopcock *G*. The pulsometer oil pump was run by a motor and made about thirty strokes per min-

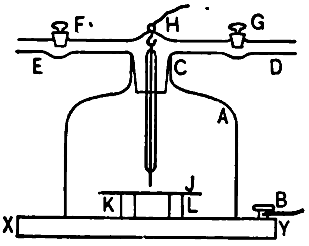


Fig. 1.

ute and by means of it I could get down to a pressure of .3 mm. A wax of rosin and beeswax was used to make the connection between the receiver and the aluminum base. The first fourteen plates were made with no account taken of pressure except that a purple light in the receiver meant a low vacuum and the pale blue light, high vacuum; direct current was used, the alternations brought about by a Wehnelt interrupter and secondary coil. This interrupter was first a thin platinum wire immersed in dilute sulphuric acid; the wire was surrounded by a hard-rubber cylinder except for its tip which dipped in the acid and could be lengthened as it wore away. It was an unsatisfactory interrupter for continuous work, since it could be run for only a minute or two at a time, then would sputter and cease working. However, if rested for a moment and thus allowed to cool, it would again work satisfactorily for a minute or two; thus a summation of effects could be obtained. Later, a solid stick of platinum was substituted for the fine wire and could be used consecutively for an hour or more at a time and in this respect was all that could be desired. But even with the platinum stick interrupter, the current density would change as the point wore away and could not be measured with any accuracy, therefore, in the end the Wehnelt interrupter and coil were given up entirely and a 2,000-volt direct-current dynamo used whose current could be accurately measured at any time. Another improvement consisted in connecting the receiver directly to a mercury pump so that lower pressures could easily be obtained and by connecting the oil pump to the mercury pump, the air could be removed from the receiver quickly and with ease — the pressure was read from a McLeod gauge connected to the mercury pump.

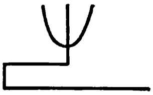
Viewed through the receiver, the glass plate could be watched during the course of the deposit and the general method of formation appeared as follows: A brown spot formed directly under the cathode; this changed gradually into reddish brown, increasing in size; then blue appeared at the center edged with red and beyond the red the brown, later blue increased in area and turned to red, indicating the starting of the second set of colored rings.

It soon became evident that time of discharge and distance between cathode point and glass plate were closely related; the closer the point to the plate, the shorter the time taken to get good colors and conversely. I also found that with the plate close to, say within 2 mm. of the cathode, the rings were narrow and of small diameter. As the distance was increased the rings spread out in area, became broader and of larger diameter. By varying the distance from 2 to 10 mm., the outside diameter of the rings could be increased from a few millimeters to several centimeters. This was true, whatever the form of cathode used. Also, on changing my cathode from coarse to fine wire, the rings became narrower and of smaller diameter.

I soon found that pressure played an important part in the formation of the rings and, after the first few films, kept a strict account of that factor.

In my early work I obtained many films that at the time of making could not be accounted for, but showed typical aspects after finding the important part that pressure and distance played. I frequently obtained dim rings, now and then a granular deposit instead of the smooth coating generally gotten and a particular kind of film showing a transparent center surrounded by a black irregular ring often puzzled me, for I was soon led to see that good colored rings had two characteristic appearances. One type showed a faint yellow tinge at the center, the other colored rings were practically transparent and beyond the colors was a wide absolutely transparent zone bounded by a fine black deposit. The other type of good colored rings showed brilliant colors and were absolutely transparent. To account for these two types and to explain variations from them, it was necessary to make many films under varying and measurable conditions.

After the cathode had been used for a time, a heavy platinum coating would collect on the glass surrounding the platinum tip. As this increased, the cathode glow would bend up about the glass, away from the tip. When this occurred, it was hopeless to accomplish anything without great waste of time, for the discharge was made very slowly and most irregularly and the best thing to do was to stop and clean off the glass.

New forms of cathodes were tried. A platinum sphere fused on the end of the heavy platinum wire gave rings like those produced by the platinum point. By varying the distance between cathode and plate, the same peculiarities in size of ring was noted as with the point cathode. I tried a cathode made of thin platinum wire bent into a circle with the plane of the circle horizontally above the glass plate. The point of joining of the circle to the supporting stem always produced a little distortion of the inner rings; but, in general, under the circular opening of the cathode there was a uniform area of color; the rings were under the wire and followed in outline the bending of the wire; the deposit directly under the wire was thickest, showing a brownish color. In any vertical section of such a cathode, different points of the wire are at different distances from the plate and in consequence the rings farther from the wire are broader than those more directly under the wire. A lack of parallelism between the circle cathode and the plate was indicated by a crescent that occurred in the rings. I gradually bent the circular cathode down until it stood vertically over the plate. Plates were made with the circle at various angles with the vertical. These plates showed the following characteristic; about that part of the wire nearest the plate, the rings were narrowest, taking an elliptical form, the lack of symmetry being on that side where the circle was farthest from the plate. This distortion decreased as the angle made with the vertical was decreased, until when the cathode stood with its plane perpendicular to the plate, all the ellipses were symmetrical. In this series of experiments, there existed in the intermediate stages what might be called a total effect and an effect due to that part of the cathode nearest the plate — the total effect being shown by the bounding elliptical rings and the special effect in the distorted and eccentric ellipses within. When the circular cathode hung perpendicularly to the plate, the special effect merged into the total effect and the plate was covered with perfectly symmetrical ellipses. After observing that an elliptical cathode gave ellipses and a triangular cathode, triangles, I tried for side effects given by the different cathodes standing my plate vertically in the receiver and near to that portion of the cathode to be investigated. Bending my circular cathode, so that its plane stood vertically and also in such a way that the effect of the supporting stem was eliminated, I obtained on a vertical plate, parallel to the cathode plane, circular rings and on a vertical plate at right angles to the cathode plane, elliptical rings as would be expected. With the elliptical cathode, ellipses were formed whether the vertical plate was placed opposite the side of least or greatest curvature, though, while in the first case, the ellipses were long and narrow, in the second case, they were almost circular; the side effects for the knob cathode were always circles. With a cathode shaped, thus,  and a horizontal plate, I obtained long, narrow ellipses, the length of the ellipse depending on the length of the wire and the width of the ellipse on the diameter of the wire; a plate placed vertically at the left hand end received ellipses and at the right hand end, namely the point, circles were obtained. The same kind of ellipses were obtained from a circular cathode hung horizontally and a vertical plate, no matter where the plate was placed, as in this case the curvature is everywhere the same.

Any change in form of cathode produced a corresponding change in form of rings and in each case, the deposit under that part of the cathode nearest the plate showed a yellow hue; beyond the colored rings was a transparent zone following the outline of the rings and beyond this zone an even black deposit. As previously noted in the case of the circular cathode, it was found that in all cases where the wire was bent into various shapes, a lack of parallelism between the plane of the cathode and the plate was indicated by a crescent of color among the symmetrical rings. Other sources of distortion of rings occurred when the discharge passed to the aluminum supports, when the plate was too small and did not cover the supports, and also when there were irregularities on the cathode. Blemishes sometimes appeared due to testing the discharge at high pressure, especially when the current was strong. In bringing the plate close to the cathode, particularly in obtaining side effects, a portion of the cathode would touch the plate and even if at first the cathode was not touching, it was noticed that as soon as the discharge passed, the cathode would be attracted to the glass and touch it througout the interval of film formation. This touching could always be traced by a transparency of the plate where the contact was, every other part of the plate having a deposit.

From experience with trying to get a half film of platinum on an interferometer plate, working twenty-four hours with the lowest pressure the oil pump would give and getting rectangular rings on the plate (like the shape of the rectangular cathode used), I realized the importance of pressure, so put my receiver on a mercury air pump with which I could obtain pressures of any value desired. I wished to find whether a low pressure produced a uniform field and no color as Mr. Langden had found.[1] With a knob-cathode at a very short distance from the plate and a pressure of about 0.1 mm. I obtained a transparent center surrounded by a black ring and no color. On using a pressure of 1.28 mm. and the same distance (2 mm.) I obtained in three minutes beautiful colored rings, showing the brown tint characteristic previously noted. Taking a given distance, I tried the effect of altering the pressure, using 1.28 mm., 0.9 mm., 0.6 mm., 0.3 mm. and 0.1 mm. pressures. I obtained colors until 0.3 mm. pressure was reached at which there was a heavy deposit, showing a trace of ring formation on the back of the plate. At 0.1 mm. pressure, there was but a slight deposit, center transparent, no color. I then tried altering the distance but taking the same pressures used before. All the charateristics previously noted were obtained. At 0.3 and 0.1 mm. pressure no colors were found but heavier deposits than for the shorter distance. Thus, when the Wehnelt interrupter was used, the minimum pressure for rings seemed to be about 0.3 mm. Then I tried to find the maximum pressure for ring formation taking a fixed distance and varying the pressure from 0.1 mm. as high as I could go and still get color. At 3 mm. pressure there was considerable trace of color, though the deposit was irregular. For good ring formation 2 mm. seemed the maximum pressure when the Wehnelt was used. So I could state that using this interrupter the minimum pressure for rings was 0.3 mm., and the maximum pressure about 2 mm. On using the 2,000-volt dynamo current, these limits were extended, particularly in higher pressures.

It was then clear how Mr. Langden, always working at pressures below 0.1 mm., had always obtained uniform platinum films while the pressures I used (usually exceeding 0.1 mm.) had resulted in colors. Also the explanation of the tiny transparent center, surrounded by a black ring, was clear. This was always obtained at pressures under 0.1 mm. and when the glass was close to the cathode; thus, the plate being within the cathode dark space, received scarcely any of the deposit. On the other hand, at pressures under 0.1 mm., when the distance between cathode and plate was increased, I obtained a heavy, uniform film. However, whenever color was obtained, I found that the cathode dark space had no effect upon my films. When the distance between cathode and plate was small I could get as good rings as for a great distance, though in the first case the plate was far within the cathode dark space and far outside of it in the other case. Also at a pressure of 12 mm., where, using the dynamo, good rings were obtained, there was no light in the receiver except a purple glow about the knob.

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[1] Electrical Resistance of Thin Films Deposited by Kathode Discharge, A. C. Langden, PHYSICAL REVIEW, Vol. XI., July-August, 1900.

As the pressure is increased from .05 mm. up to 5 mm. the following stages may be traced in the films formed between these limits; at .05 mm., the lowest pressure used, there was a heavy platinum deposit; at 0.1 mm. a uniform deposit, but more under the cathode and less spreading than for .05 mm. pressure; at 0.2 mm. a slight trace of color was noticed in the uniform deposit, more frequently on the back of the glass plate; at 0.3 mm. colored rings were formed that were practically transparent and this held up to 1 mm. pressure; at 1 mm. the appearance was that of colored rings slightly yellowish in tint surrounded by a transparent zone and beyond the zone an even black deposit. At 2 mm. pressure, the rings were very perceptibly smaller, the transparent zone correspondingly contracted and the outer black deposit thinner and more transparent; from 2 mm. upward, the decrease in size of rings and transparent zone continued and the increase in the transparency of the film also continued. At a pressure of 12 mm. the rings were very small and practically transparent with no other trace of deposit. The above account applies to films, when the distance between the cathode and plate is from zero to six millimeters. When the distance is ten millimeters, a similar description applies until 1 mm. pressure is reached. At that point, the large rings began to decrease and the transparent zone was small, a greater increase of pressure resulted in a uniform black film and no color. This heavy deposit continued up to near 2.5 mm. pressure then grew thinner as the pressure was increased, ultimately disappearing. (I had previously noted that often, after a deposit, there was a heavy black coating on the aluminum base of the receiver; this coating was more noticeable when a small glass plate was used, thereby exposing more of the base to the rays; at the same time on the glass, colors, only appeared.) It seems then that transparency is characteristic of low pressure, brown color and boundary zones for a moderately low pressure. For moderately high pressure, two cases exist, depending on the distance of the plate from the cathode and resulting in smaller rings and increase of the black deposit for the shorter distance and heavy black deposit, showing no color for the greater distance. Again for very high pressure there is very little deposit, whatever the distance. The lower the pressure and the greater the distance, the more transparent is the film within the range for good ring formation. The changes occurring in a film, as the pressure is increased from .05 to 5 mm. may be summed up thus: an even black deposit gradually gives way to colored rings; shortly before 1 mm. pressure is reached, the black deposit again appears at the edges of the plate; with greater increase in pressure, the rings decrease in size and the black deposit creeps in toward the colored area, reaches a maximum and at high pressure disappears. When the distance between cathode and plate is small, the colors begin at a higher pressure than in the case where the distance is great and the black deposit at high pressures is not so heavy, nor does it conceal the rings completely. For all distances, the appearance at 1 mm. pressure is characteristic and this may be called the critical pressure. A disturbing element in comparing corresponding films at different distances was due to the glow not being strictly confined to the cathode. If it ran up the glass of the cathode or if a discharge occurred at the top of the receiver, the rings were smaller and took a longer time in formation.

I see no possible explanation of this phenomenon on the basis that the even, black deposits are obtained when the plate is just at the edge of the cathode space, for, while it may apply to results obtained at low pressure, it cannot explain why at high pressure and great distance an even deposit is obtained. Again, as pressure increases and the glow decreases, the plate nearest the cathode would ultimately touch the edge of the cathode dark space and receive the even deposit which is contrary to the results obtained. It is a curious fact that, for a distance of 10 mm. an even film may be obtained either at .2 mm. pressure or at a pressure ten times as great.

In comparing those films made by using the Wehnelt interrupter with those made by the current from the two thousand volt dynamo, it is interesting to note that the two classes are really one and the same; for a given pressure and distance, the appearance of the resulting film is the same in either case.

The attempt was made to arrive at the same stage with each film; let us say the starting of the second set of rings. This could be observed from outside the receiver when the light was good. One could see the brown spot form under the cathode, could see it turning to red, then to blue and then to brownish red again, thus indicating the starting of the second set of rings. Under these circumstances, it was possible to make comparison of the time taken at the different pressures to reach this stage. Although one must keep in mind the fact that an increase in distance between cathode and plate means an increase in time, since the size of the rings is correspondingly increased, nevertheless one can say that in any set of films where the distance is unchanged the time taken to reach the given stage of film formation is the same from the lowest pressure giving rings up to the pressure where the even deposit starts to decrease. Beyond this pressure, the time is increased. Suppose the time of formation between 0.3 mm. and 2 mm. pressure is ten minutes, the time taken to reach the same stage in the rings from 2–5 mm. pressure is almost twenty minutes and beyond 5 mm. pressure, the time is enormously increased, two hours and a half being necessary for a film at 12 mm. pressure. In this connection, it should be stated that films made with the interrupter took a longer time than exactly similar ones made by the current from the dynamo.

To be able to measure the current flowing through my receiver and the fall of potential between anode and cathode, at any chosen pressure, I put an ammeter reading to .001 ampere in the main circuit and a static quadrant electrometer between anode and cathode. Beginning with the highest pressure used and letting the discharge pass through the receiver, I read the current and voltage for that pressure; taking a stroke of the pump, I again read the three corresponding values. In this way I proceeded by steps to the lowest pressure used in the work. The discharge passed continuously between cathode and plate during this experiment, the accompanying curves give the relation between pressure and voltage and pressure and current respectively and show that down to a pressure of about 1 mm. the current and also the voltage is practically constant; between 1 mm. and the lowest pressure used, a slight decrease in pressure is accompanied by great increase in potential and corresponding decrease in current. At four separate times such a series of values were taken and curves constructed (Figs. 3 and 4). In two trials the voltage was constant at about 650 volts and the current constant at .005 ampere until a pressure of 1 mm. was reached; then the current fell steadily to .001 ampere and the voltage rose to 1,950 volts; in a third trial, starting with .004 ampere and 600 volts, both factors remained constant until the pressure was decreased to 1 mm.; between 1 and 0.5 mm. pressure the change was slight, but below 0.5 mm. the current fell to .001 ampere and potential rose to 1,750 volts; a fourth trial started with a current of .001 ampere

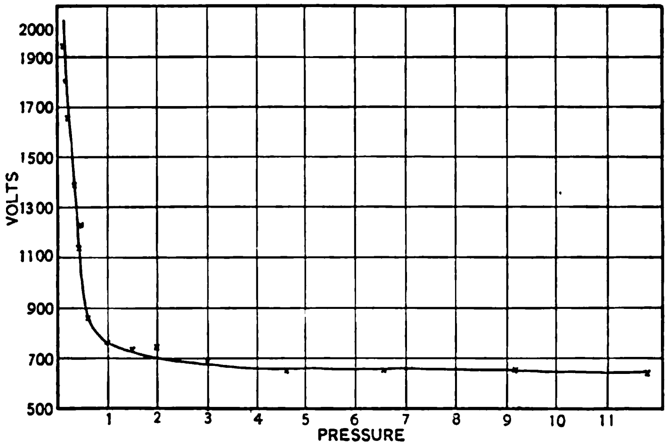


Fig. 3.

and voltage of 550, both remained constant until 0.5 mm. pressure was reached; then came the sudden drop of current to .0001 ampere and rise of potential to 1,730 volts. Evidently the critical point in pressure for these platinum films is lowered by using a lower voltage and current. If the object is not the lowering of the critical pressure, it is of course far better to use a stronger current and shorten the time of deposit. The current usually used in depositing these films was .004 ampere. In comparing the films by reference to these curves, one finds that the uniform films at pressures below 0.1 mm. are formed when the curve is practically vertical; that the colored rings showing greatest transparency and free from all uniform deposits are made when the curve shows a rapid decrease of voltage and rise of current and that the deposit is heavier for those films made at pressures above 1 mm. where the curve exhibits itself as a horizontal line. Beyond 3 mm. the decrease in deposit is due to increase in pressure as indicated by the slight glow about the cathode. From observing the curves, I could understand why in the region of pressures below 1 mm., there would be great fluctuations of voltage, for the small increase in pressure due to gases coming off the cathode at the time of dis-

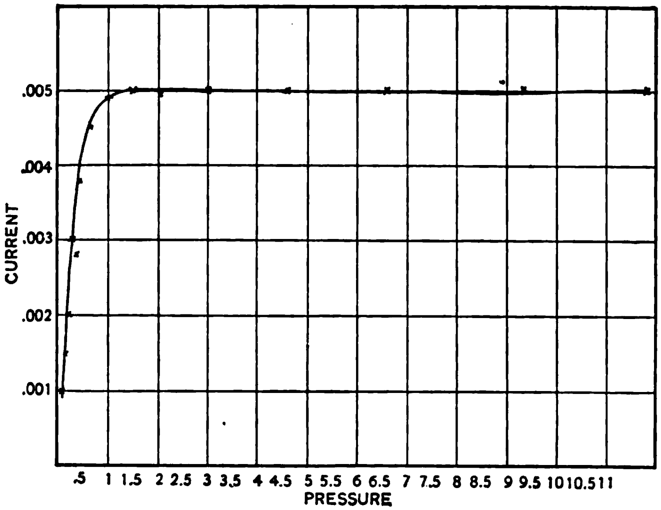


Fig. 4.

charge. Also if a discharge took place at the platinum hook on which the cathode was suspended, the voltage would drop and the current rise, and if, because of the coating with platinum of the glass about the cathode, the glow ran up the glass, again a change would occur. In connection with these curves it is interesting to note that the test plate used in such an experiment became covered with very large rings showing six or seven alternations of color and the deposit of considerable thickness, thus increase of time of deposit would result in the formation of many rings spreading over the surface of the plate.

In order to prove that the colors would form when a gas other than air was used, I arranged to make the deposit in hydrogen. In the first set of films made by the interrupter, I introduced into the receiver hydrogen generated by the action of acid on zinc and dried by passing it through sulphuric acid and phosphorus pentoxide. I pumped this gas through the receiver three or four times before the discharge passed and thus I made a half dozen plates at varying pressures, in each case rings were formed just as in the case of air. To make sure that I had gotten rid of the gases occluded by the cathode and on the walls of the receiver, I resolved to let the discharge using current from the dynamo pass for some time until the pressure of the hydrogen was stationary as indicated by the gauge. Since, with the preliminary discharge, the glass surrounding the cathode would become coated with platinum and in consequence the glow would bend up about the coated glass, it was necessary to protect the glass during the preliminary discharge. Two pieces of mica were taken and bent so as to surround the cathode above and below, shielding the glass about the cathode and the glass plate. Each of these pieces of mica being wound externally with iron wire was removed when the time came by a magnet outside the receiver. These covers having been fitted around the cathode and the receiver made air tight and connected with the pump, the air was exhausted to a low pressure, C. P. hydrogen was admitted and the pressure again reduced. In this way, hydrogen was admitted three times; then the discharge was allowed to pass for two hours. This process was again repeated and during the second discharge, the gauge was watched. At the end of two hours, when the gauge showed no increase of pressure, the mica covers were removed from without and the discharge allowed to pass onto the glass plate for twenty minutes, the pressure being 1 mm. The rings were like those obtained at the same pressure in air.

I had made attempts to find the thickness of the films by the micrometer calipers, the measurements, however, were of no value even for thick films because of the uneven thickness of the glass and for thin films I obtained negative values.

I then tried weighing a microscope cover glass, putting on a thin film, reweighing and calculating the average thickness of the film from weight, average diameter of circles and density of platinum. By this method, I found the average thickness equal to .000136 mm. or the thickness of Newton's first bright ring (.000142) approxmately. As this was an attempt to discover how the platinum was deposited on the plate and as I had found that direct observation under the microscope gave me interesting results, I abandoned the weighing method and examined the films one by one under a microscope. When traces of particles were found, the plates were prepared with Canada balsam and cover glasses for use with a high power oil immersion objective. The microscope was then put in front of a lantern and the magnified image obtained on a screen. By running the plate horizontally and vertically, it was possible to examine the whole area and photograph any part of it. Some photographs were taken with objects magnified to 2,000 diameters, others to 2,500 diameters. A film made at a pressure of .2 mm. showed a field of perfectly spherical particles varying in diameter from .0005 to .0009 mm. Apparently there was no symmetrical grouping of particles; some were alone, others in large or small groups and here and there an area quite free from them. Each globule was surrounded by a halo. In other films I found many clusters in various stages of development, several globules collected in a faint halo-like area; again a union of many into a rather irregular crystalline appearing area and finally the merging of masses of these crystalline areas into a large solid appearing mass, surrounded frequently by a brown fringe; the photographs illustrate these stages. The thick films shut off most of the light from the lantern and were uniform except where a tear showed the existence of a continuous yellow layer or here and there a crystalline area appeared. Since many of the thin films appeared transparent and the thick ones showed an even yellow deposit, my photographs, for the most part, represented those films where the particles had not yet clustered together to form a continuous film or were taken on the outskirts of the colored area, where the stages of formation could best be observed. Frequently crystalline areas appeared on a uniform field, indicating that particles had been thrown off irregularly after the film proper had formed.

The following explanation seems to fit the observed facts: during the first few minutes of the discharge the platinum thrown off from the cathode is in the form of globules, separated from each other or slightly grouped, hence the deposit appears red; as the discharge continues more globules are deposited, there is a joining together of the groups and the deposit appears blue, edged with red. This, then, would explain the formation of the first set of rings; the center made up of particles close together, the outskirts containing only separate particles. This process is repeated, the thin, transparent film serving as a base for deposit; again particles increase directly under the cathode, first, separated from one another and we have red, then uniting together and we have blue; thus a second set of rings have been formed. As this continues, the rings spread out over the surface of the plate and it is evident why extremely thin films and the outer boundary of the colored area, alone exhibit the separate particles.

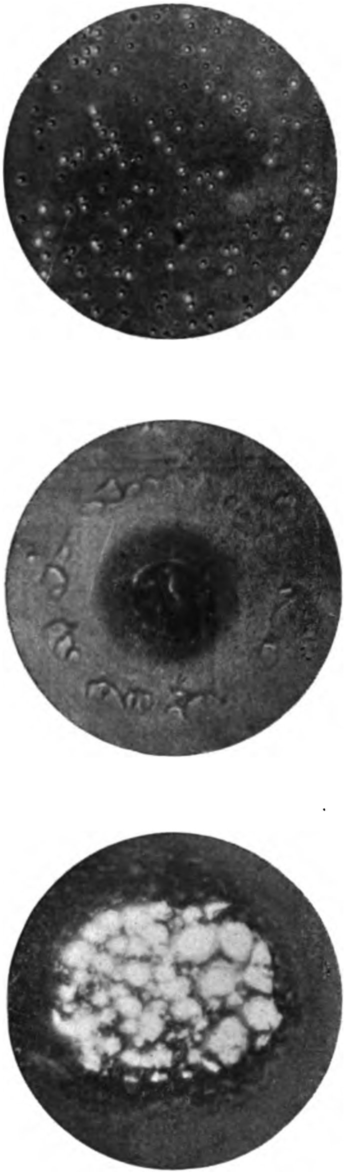
The particles may be of different sizes; the change in color depends not on the size, but on the grouping of the particles.

It is my intention to examine films showing the first red color and compare with others in which blue first appears; to investigate farther into the formation of even films at great distance and high pressure and to examine the phenomena produced by a cathode of material different from platinum.

I wish the opportunity to express my gratitude to Dr. Hallock for making this investigation possible for me at Columbia University and for his great liberality and kindness to me throughout the accomplishment of the work. I am also greatly indebted to Dr. Davis, Dr. Tufts, Dr. Pegram and Dr. Forbes for valuable advice and for assistance many times.

VASSAR COLLEGE.

PLATE I.
(To face page 40.)



Color in Platinum Films.
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THE MAGNETIC ROTATION OF SODIUM VAPOR.

By R. W. Wood and H. W. Springsteen.

Introduction.

In 1811 Arogo[1] discovered that rotation of the plane of polarization occurs when plane polarized light is transmitted through quartz in the direction of its optic axis. This was followed by the careful investigations of Biot,[2] which led him to the deduction of his three well-known laws. That the phenomenon was not confined to solids alone, but occurred also with liquids and gases, was soon made evident by the work of Biot, Sir J. Herschel, Brewster, Faraday and others. Then followed Faraday's discovery[3] that the plane of polarization is rotated by isotropic substances when placed in a magnetic field.

After the discovery by Fox Talbot,[4] about 1840, of the existence of anomalous dispersion, this phenomenon was looked for in the rotatory dispersion of optically-active substances. Biot,[5] Arndtsen,[6] Landolt,[7] Nasini and Gennari,[8] Cotton[9] and others observed anomalous rotatory dispersion in various natural active liquids.

It was natural to expect that this anomaly might also exist in magnetically active substances; several investigators have studied various substances with results not altogether concordant. Becquerel[10] in 1880 observed the effect in oxygen, but others have been unable to confirm his results. Macaluso and Corbino[1] worked with sodium vapor and found that the rotation was positive, and abnormally great, on each side of the *D* absorption bands, but had a small positive value inside the band. Zeeman[2] also, with a flame between magnet poles, investigated the rotation with highly rarified vapor in the vicinity of the *D* lines and obtained a positive rotation just outside the two *D* lines and a very great negative rotation inside each of them, or rather between the components into which the magnetic field divides the line.

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[1] Arago, Oeuvres Completes, Tom. X., p. 35, 1812.

[2] Biot, Ann. de Chimie et de Physique, 1815.

[3] Faraday, Experimental Researches (XIXth series), Vol. III., p. 1; Phil. Trans., p. 1, 1846.

[4] Talbot, see Tait's Light, 196, and Proc. Roy. Soc. Edinburgh, 1870–71.

[5] Biot, Ann. de Chimie et de Physique (3), 10, p. 5, 1844.

[6] Arndtsen, Ann. de Chimie et de Physique (3), 54, p. 403, 1858.

[7] Landolt, Beibl., 5, p. 298, 1881.

[8] Nasini and Gennari, Zeitschr. fur phys. Chemie, 19, p. 113, 1896.

[9] Cotton, Ann. de Chimie et de Physique (7), 8, p. 347, 1876.

[10] Becquerel, Compt. Rend., 90, p. 1407, 1880.

Results published by Schmauss in the Annalen du Physik during the year 1903 appeared to show that the rotatory dispersion is anomalous in the vicinity of the absorption band. He worked with alcoholic solutions of the analine dyes, and with didymium glass, obtaining curves not unlike the anomalous dispersion curves of these substances. His work was repeated by Bates[3] who failed to find any effect whatever due to the addition of the dye, and one of the present writers, has been unable to observe any trace of magnetic rotation in the case of thin plates of solid cyanine in very intense magnetic fields, although a saturated solution of praseodymium chloride appears to show the effect.

In the case of sodium vapor we know positively that the rotation is not anomalous, having the same value for wave-lengths symmetrically situated to the right and left of the *D* lines.

The subject is of much interest theoretically, for the rotation formula developed from the hypothesis of molecular currents[4] calls for an anomalous effect, while the one obtained by considering the "Hall-effect," *i. e.*, the ponderomotive force exerted upon an electron moving in a magnetic field, represents, qualitatively at least, the condition found in the case of sodium vapor.

It was with a view of testing this formula quantitatively that the experiments about to be described were undertaken.

To test a formula we require observations over a fairly wide range of wave-lengths.

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[1] Macaluso and Corbino, Compt. Rend., 127, p. 548, 1898.

[2] Zeeman, Proc. Roy. Acad. of Amsterdam, 1902.

[3] See Annalen du Physik., Dec., 1903.

[4] See Drude's Optics.

In the course of some work upon the dispersion of the vapor of metallic sodium, it was found by one of us, that the vapor possesses an enormous rotatory power, even for wave-lengths considerably removed from the *D* lines, when placed in a strong magnetic field.

It was at once recognized that by employing this medium, the rotatory dispersion formula

$$\delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\lambda^2}{(\lambda^2 - \lambda_m^2)^2}\right)$$

could be tested.

That it represents the dispersion qualitatively is clear from the occurrence of the term $(\lambda^2 - \lambda_m^2)^2$ in the denominator, for $\lambda^2 - \lambda_m^2$ changes sign when we cross the absorption band, and it is this change of sign which gives us the anomalous dispersion. In the present case, however, the squaring of the term gives us the same sign on opposite sides of the absorption band, which calls for a dispersion curve of the type shown in Fig. 1. A curve of this type was obtained by Cotton, but his observations were made with flames, and the effect could only be traced to a very small distance to the right and left of the *D* lines.

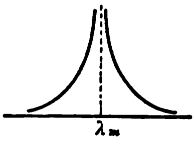

Fig. 1.

We can modify the above formula somewhat in the case of sodium vapor as will be shown later on in the paper.

APPARATUS AND METHOD.

The sodium vapor obtained by heating a salt of sodium in a flame is necessarily very rare, and with such a vapor as is well known, the rotation only very near the *D* lines is perceptible. In order to obtain greater rotations it is obvious that denser vapor must be employed. This was accomplished by heating with a Bunsen flame pure sodium in an exhaused glass tube. This tube, of hard Jena glass, had a length of 25 cm. and an inside diameter of 1.3 cm. Over this and occupying a position midway between the ends of the glass tube was a brass tube 8.2 cm. in length and of such a diameter that it would slide easily over the glass tube. A solid cylindrical piece of pure sodium of the same length as the brass tube, and having a diameter of 0.6 cm. was prepared in the following way. A good-sized piece of sodium was melted in an iron crucible over a Bunsen flame, and the molten metal poured into an iron cylinder. This cylinder had a tight fitting iron piston which, when pressed in by squeezing it in a vice, forced the sodium out through a small hole in the end, and the desired length being then cut off. The sodium stick was then placed in the center of the glass tube as quickly as possible to prevent the moist air from coming in contact with it, and the ends of the tube closed with thin pieces of plate glass, cemented on. The glass ends were tested in the magnetic field employed for the experiment, but no rotation due to them could be detected.

Directly over the sodium and inside the glass tube was a thermos element made of iron and constatin fused together; the terminals passing out through a fine glass tube at one end of the sodium tube. Passing through the other end was a tube of small diameter which was connected to an air-pump and sealed off after exhausting the tube. The vacuum used was about one tenth of a mm. of mercury. The sodium tube was then placed inside a Ruhmhorff magnet as shown in the figure, so that the part of the tube containing the sodium was between the poles of the magnet. The magnet possessed the usual nicol prisms, one at each end, the analyzing one being provided with a rotating arm and scale which could be read to tenths of a degree. The wires from the thermo-

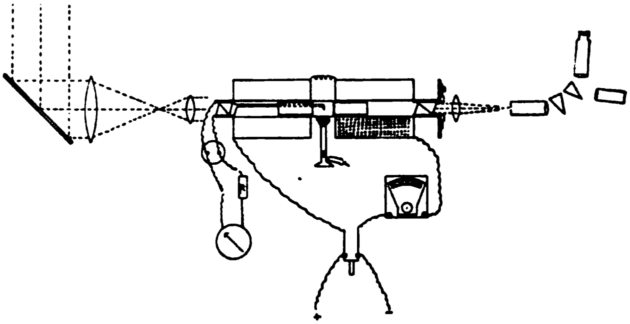

Fig. 2.

element passed out alongside the latter nicol, and communicated with a galvanometer and two other thermo-elements, one of iron and copper and the other constantin and copper. These two elements were placed side by side in a kerosene bath and kept at constant temperature. Directly beneath the center of the brass tube was a Bunsen burner, the height of which was so regulated as to produce the required temperature of the vapor, as determined by the scale-reading of the galvanometer. The brass tube served to distribute the heat from the flame more evenly than could otherwise have been done, and by this means the vapor was kept at a very uniform density.

A 110-volt circuit was connected to the magnet through a double-knife switch, rheostat and ammeter. Since the magnet coils were made of very large wire, a heavy current could be used and the rheostat was adjusted until the current was 35 amperes, and all the observations were made with this current through the magnet. The current, of course, heated the magnet somewhat, but after a short time this heating became fairly steady and with a constant current, the variation in the field-strength introduced no more error than the errors of observation. The strength of the field was determined by measuring the rotation for D light which a tube of carbon bisulphide, 8.2 cm. in length, produced. The average rotation obtained was 16°.0. Assuming 0.042 in minutes of arc as the value of Verdet's constant, this rotation of 16° corresponds to a field strength of 2,790 C.G.S. units.

Considerable difficulty was experienced in trying to obtain a sufficiently intense beam of light. The light had to pass through various optical parts and also the dense vapor so that finally only a small percentage of the incident light succeeded in getting through the apparatus. As first tried, the light from an arc was brought to a focus just in front of the polarizing nicol, and after passing through this and the sodium vapor, it could be completely extinguished by the analyzing nicol. Just in front of the analyzing nicol was placed a transmission grating of 14,000 lines and when the nicols were parallel, a bright spectrum was produced in the first order. When the nicols were crossed, the spectrum entirely disappeared. The sodium was now slowly heated, and with the nicols parallel, the *D* absorption band slowly appeared, becoming wider and wider as the vapor became denser.

The nicols were now crossed and when the current was turned on, the light was immediately restored for a considerable distance on each side of the *D* absorption band. It also seemed as if there was a restoration of the light in the part of the spectrum corresponding to the position of the fluted absorption bands, but it was not possible to be sure, with this arrangement of the apparatus. If the analyzing nicol was now slowly turned in a direction which indicated a positive rotation, there appeared two broad black bands, one on each side of the *D* band. As the nicol was rotated more and more, these bands narrowed up moving closer and closer to the edges of the *D* band, until finally they reached it. This showed that the rotation was positive on both sides of the *D* band, and by the readings of the nicol, it was seen that the rotation was very great close to the edges of the *D* band, but that it rapidly decreased for points further and further away. By using less dense vapor and a reflection grating mounted on a spectrometer, it was possible to see in the second order that the rotation was also positive between the two *D* lines, but the light here was too faint to permit of a very accurate determination of its amount. It was now necessary to devise some means of determining the wave-length cut out by the black band as the nicol was rotated. To effect this, the light from the arc was focussed on a slit and then made parallel by a collimating lens before it passed through the first nicol. After emerging from the second nicol, it then fell upon a plane reflection grating and into the telescope of the spectrometer. Then the light from a helium tube and a mercury tube was sent through at the same time by means of a small right-angled prism placed on the slit of the collimator, with the intention of using their characteristic lines as reference points from which to measure wave-lengths. But it was found impossible to make the lines appear sufficiently bright and the use of these tubes was abandoned.

Next the sunlight from the heliostat was substituted for the arc, with the hope that the Fraunhofer lines might be sharp enough to be used. But these too, proved to be too indistinct to be employed.

The next method tried was the following: sunlight was focussed on the slit of a monochromatic illuminator and light of the desired wave-length then transmitted through the first nicol, the sodium and the analyzing nicol in turn. The latter was then rotated until the light appeared to the eye, to be entirely extinguished. By this means the rotation for different wave-lengths was obtained at some distance on either side of the *D* band, but when settings were made in its vicinity, the source of light could not be made monochromatic enough, even with the slits of the monochromatic illuminator very narrow, since the magnetic rotation in this vicinity is very great, and although the nicol might be turned so as to extinguish light of one wave-length, light of other wave-lengths would still pass through. With this arrangement, however, the rotation was measured for wave-lengths rather distant from the *D* band and readings were taken until the restored light became too feeble to make the settings accurate.

For the vicinity of the *D* band another method was found which proved very satisfactory. A beam of sunlight from a heliostat was sent through the nicols and sodium tube and focussed upon the slit of a two-prism spectroscope which possessed a resolving power sufficient to separate the *D* lines. By this means the Fraunhofer lines were in sharp focus. An auxiliary scale reflected into the field of view, appeared superposed on the solar spectrum.

With the nicols parallel and the vapor of the right density, not only was the *D* absorption band visible, but also the red and blue channelled absorption bands were very strong. When the nicols were crossed, the field was dark, but when the current was turned on, the spectrum brightened up, not only on each side of the *D* band, gradually shading off in intensity, but also in the red and blue-green. As many as eight distinct red, and eight blue, bright lines were counted. These bright lines apparently coincided with the red and blue absorption bands of sodium vapor, and showed conclusively that the red and blue absorption bands have also a very marked effect on the magnetic rotation.

The bright blue lines due to magnetic rotation were much fainter than the red and it was noticed that when the vapor was of small density, the bright lines in the red appeared, but no trace was seen of those in the blue-green region. This indicates that the rotation is greater for the red lines than for the blue ones. The absorption lines appear, however, in the greenish blue at a smaller vapor density than that necessary for the appearance of the red absorption bands.

The nicol was rotated and the position of the black bands noted with reference to the spectroscope scale. The position of the nicol was read and the temperature of the vapor recorded. The readings were always taken with a constant current through the magnet. Throughout the experiment the temperature of the vapor remained nearly constant. It is clear that the black bands mark the wave-lengths, for which the rotation is represented by the angle through which the nicol has been turned from its original position of extinction.

The results obtained are recorded in the following table, which is for wave-lengths on the green side of the absorption band.

λ	δ		
	Observed.	Calculated.	
5,886	2,371°	2,285	$\lambda_1 = 5,890$
5,884	1,185	1,016	
5,876	247	186	
5,875	205	162	
5,870	107	91	
5,861	49	40.6	
5,844	14.8	15.2	$\lambda_1 = 5,893$
5,835	10.8	10.9	
5,820	6.5	6.9	
5,805	4.8	4.8	
* 5,770	2	2.5	
* 5,725	1.4	1.4	
* 5,690	1.2	1	
* 5,660	1.0	—	
* 5,630	0.6	—	
* 5,600	0.4	0.5	

The readings marked with an asterisk were made with the monochromatic illuminator, the others by observing the position of the dark band in the continuous spectrum, which appears the moment the second nicol is turned from its position of extinction. The high values for the first five wave-lengths, were obtained by making observations with a grating, using a vapor of small density, and then enlarging them to the scale of the density of the vapor used in the other experiments. The rotations on the red side of the *D* lines are similar for wave-lengths similarly located, in other words the curve is symmetrical. The complete curve is shown in Fig. 3.

It is probable that the complete curve is far from accurate as a whole, for it was constructed from different sets of readings. Moreover the density of the vapor is apt to change during the time occupied in observing and recording a single series.

At the present time experiments are being made by one of us with a photographic method, which it is expected will yield far more accurate results.[1]

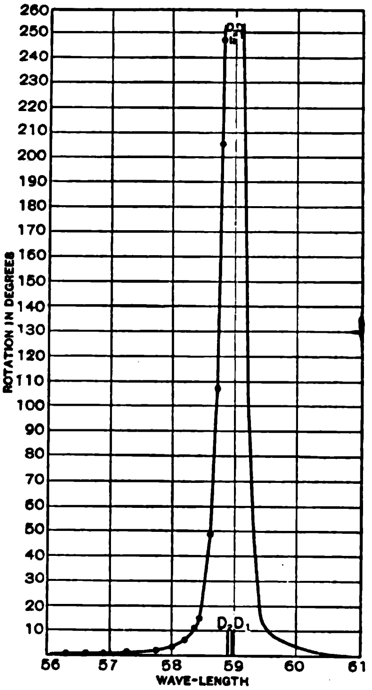

Fig. 3.

PROOF OF THE ROTATORY DISPERSION FORMULA.

In the complete formula

$$\delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\lambda^2}{(\lambda^2 - \lambda_m^2)^2}\right)$$

the first term in the parentheses represents the effect of electrons with periods in the ultra violet. The dispersion of sodium vapor has been shown by one of the writers to be represented by the formula

$$n^2 = 1 + \frac{b\lambda^2}{\lambda^2 - \lambda_m^2},$$

in other words the electrons which cause the *D* lines are alone operative. We can thus safely assume that the rotation is influenced only by these same electrons, in other words we may neglect the term a/λ^2. The effects contributed by the absorption bands in the blue-green and red can be left out of account as they are but very small. Moreover in the case of sodium vapor n does not differ greatly from unity, except very near the *D* lines. We can therefore write the formula for the rotation

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[1] These measurements have been repeated with a 14-foot concave grating, not only on each side of, but also between the *D* lines. The rotating lines in the red and blue green region, to the number of 150 have been accurately measured with the same grating. The results will appear shortly in the Philosophical Magazine. R. W. W.

$$\delta = \frac{b\lambda^2}{(\lambda^2 - \lambda_m{}^2)^2}$$

and determine the constant b from a single observed rotation.

It is clear that the term $\lambda^2/(\lambda^2 - \lambda_m{}^2)^2$ will change with changing wave-length much more rapidly than the term $\lambda^2/(\lambda^2 - \lambda_m{}^2)$ (which occurs in the ordinary dispersion formula); the rotatory dispersion curve will consequently be much steeper than the dispersion curve, as will be readily seen by comparing the curve shown in Fig. 3, with the dispersion curve obtained by Wood for sodium vapor.[1] In calculating the rotations λ_m was given the mean value of the *D* lines 5,893 in the case of the remotor wave-lengths, and the value 5,890 in the case of those near the absorption. This is an approximation method of course, but it was found to work fairly well in the case of the dispersion of the vapor. The calculated results agree fairly well with the observed, except for the immediate vicinity of the *D* lines, where they are for the most part too low.

A series of readings were taken with improved apparatus, using a diffraction grating, and measuring the position of the band with a filar micrometer. These observations were made as rapidly as possible to avoid changes in the density, which, as has been already said, are probably responsible for most of the errors. The constant was calculated from the rotation observed for wave-length 5,839,

λ	δ		
	Observed.	**Calculated.**	
5,875	95°	87.2	Constant $b = 113{,}382$ $\lambda_m = 5{,}893$
5,886	36	38.7	
5,875	23	21.7	
5,839	9.5	9.5	
5,821	5	5.4	
5,803	3	3.4	

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[1] Phil. Mag., Sept., 1904.

and the observed and calculated values compared. The results are recorded in the opposite table, and indicate that the rotatory dispersion is probably represented by the formula given above.

More accurate results are expected with the photographic apparatus, which will enable the position of the dark bands to be rapidly recorded for different settings of the nicol. The maesurements can then be made at leisure.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

NOTE ON FLEETING AND PERSISTENT NUCLEI IN ENERGIZED DUST-FREE AIR.[1]

BY C. BARUS.

1. *Fog Limits of Fleeting Nuclei.* — The mean increment of nucleation, δN, per centim. of increment of pressure difference, δp, varies very rapidly as compared with the fog limit, δp_0, so long as the reference is to the interval of large variation. It makes no difference by what radiation the nucleation is produced (X-rays or other radiation), $\delta N/\delta(\delta p)$ is rapidly larger as the intensity of ionization is greater, while δp_0 becomes slowly smaller within the interval in question. Below the fog limit of air, and slightly above the fog limit of the ionized medium, the following data are typical. N_{21} shows the number of nuclei caught when $\delta p = 21$ cm., which lies within the pressure interval stated. D is the distance of the sealed aluminum tube, containing radium (.1 g.), from the fog chamber.

Radium (10,000 ×)	$D = 200$ cm.	$\delta p_0 = (20.5)$	$10^{-3}N_{21} = 1$	$10^{-3}\delta N/\delta(\delta p) = 4$
	50	20.4	5	9
	25	20.3	10	(14)
	0	20.1	18	20
X-rays.	200 cm.	20.3	10	16
	50	(20.1)	22	(24)
	10	(19.7)	45	(33)
	5	19.6	50	36

The full N curves are best given graphically. Data for the radium at $D = 100 - 200$ cm. are scarcely distinguishable from air except near the fog limit; for radium at $D = 10 - 25$ cm. they lie close together, above the former and below the data for $D = 0$. With these the X-ray effects at $D = 10 - 50$ cm. are in sequence. Thus there is general continuity between the air curves, the radium curves and the X-ray curves. As a whole the curves for N and δp are doubly inflected: relatively large nuclei are rapidly fewer in number as δp decreases, relatively small nuclei are also rapidly fewer in number as δp increases. Nevertheless the efficient nuclei of intermediate dimensions are of all sizes, while this size tends to become more uniform as the ionization is greater, *i. e.*, the slopes of the curves become steeper. Gradation is accentuated for the case of weak ionization.

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[1] Read by title at the Chicago Meeting of the Physical Society, April 22, 1905. For earlier observations see Science, XXI., p. 275, 1905; *ibid.*, XXI., p. 563, 1905; Am. Journ. Sci. (4), XIX., p. 349, 1905.

2. *Decay of Fleeting Nuclei.* — If N is expressed in thousands of nuclei per cub. centim. and the time of decay t in seconds and if $1/N = a + bt$ so that $dN/dt = - bN^2$ the datum $b = .002$ reproduces the decay curves moderately well, except at the beginning ($t < 30$ sec.), where the observed data are steeper.

3. *Generation and Decay of Persistent Nuclei.* — First exhaustion data of the generation of persistent nuclei are difficult to obtain because the coronas soon become heavy fogs, distorted beyond recognition, and the fog limits variable over wide limits often approaching vanishing smallness. The number of persistent nuclei generated varies with the time of exposure at an accelerated rate as if the nuclei themselves assisted in the generation. For instance at $\delta p = 19.7$ cm., after the times of exposure 1, 2, 3 minutes the nucleations were $N \times 10^{-3}$ 22, 77 (120), respectively.

If N be expressed in thousands of nuclei per cubic centimeter, if t is the time of decay in seconds, and if $1/N = a + bt$ (for which there is here no experimental justification, and which serves only for systematic comparison with the preceding case), the data show that $b = .000013$, *i. e.*, over 200 times smaller than in § 2.

4. *Solution of Fleeting Nuclei* (*Ions*). — Further experiments in the wooden fog chamber showed that 25–50 per cent. of the fleeting nuclei could be caught and made stable on solution. The mean datum of all results irrespective of the time interval (the effect of which within a few minutes is probably inappreciable) is a preservation of 39 per cent. on re-evaporation of the originally fleeting nuclei from the fog particles condensed on them. In the absence of subsidence of fog (which can not here be allowed for) the result would be larger. In the glass fog chamber which could be made rigorously free from leakage but in which the subsidence loss was greater, 20 per cent. persisted, while all but 2–5 per cent. were lost in 1 minute in the absence of solution. Persisting in the 1–3 minutes following evaporation was not appreciably different, indicating long periods of decay.

5. *Solutional Enlargement of the Nuclei in Dust-free Air.* — The most

interesting case observed is the marked decrement of the fog limit of dust free air producible by solution of the nuclei. Let the first exhaustion be made decidedly above the fog limit (say here at $\delta p = 23$ cm.), to obtain a corona of appreciable size. On evaporating the fog particles, let the second exhaustion be made decidedly below the fog limit (say at $\delta p = 21$ cm.). A large corona, which would otherwise be quite absent, will be observed. Within 3 minutes about 25 per cent. of the nuclei are found to persist. After 10 minutes not more than 5 per cent. were left.

6. *Cause of Periodicity.*[1] — In cases of alternations of large and small coronas, whether the persistence be attributed to electrical potential or to solution, a water nucleus is always in question. Small fog particles are caught on small nuclei near the limit of exhaustion and these evaporate and become the water nuclei available for the next exhaustion. In general there are three groups of nuclei x, y, z, concerned in an exhaustion: a group x of water nuclei from the preceding exhaustion; a group z, which will evaporate to make the water nuclei of the succeeding exhaustion; finally the group y comprising the efficient nuclei of the exhaustion in question. In case of periodicity the successive exhaustions follow the scheme

Exhaustion	1		y_1	z_1	Superior corona on y_1
	2	$x_2 = z_1$		$z_2 = 0$	Inferior corona on z_1
	3	$x_3 = z_2 = 0$	$y_2 + y_3$	z_3	Superior corona on $y_2 + y_3$
	4	$x_4 = z_3$		$z_4 = 0$	Inferior corona on z_3
	5	$x_5 = z_4 = 0$	$y_4 + y_6$	z_5 .	Superior corona in $y_4 + y_5$
			etc.		

All the details observed with alternations, are thus explained. In view of the rapidity of decay the corona will be formed on the saturation value of $y_n + y_{n+1}$.

7. *Persistence in General.*— This may reasonably be ascribed to the formation of water nuclei, a point of view carried out in my memoir on the structure of the nucleus (Smithsonian Contributions, No. 1373, 1903), but much enhanced by the data of the present investigation. The heavy rains accompanying condensation in case of the persistent X-ray nuclei, are attributable to spontaneous condensation without supersaturation, the nucleus acting under intense X-radiation like a hygroscopic solute. The same result may follow the action of ultra-violet light, as it certainly must result from the presence of phosphorus and of sulphuric acid nuclei.

8. *Distance Effect in Case of X-rays.* — The behavior of the wooden fog chamber in relation to rays coming from different distances being such as if the circumambient medium were equally energised with some-

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[1] Cf. Am. Jour. Sci. (4), XIX., p. 349, 1905.

thing recalling the character galvanic polarization, throughout, the following mean data are designed to throw further light upon this behavior. D is the distance of the bulb from the fog chamber. The exhaustion is at the fog limit of dust free air.

Fog chamber	$D=6$	50	200	600 cm.
Wood, lead-cased	$10^{-3}N=50$		50	38
Glass, walls, .3 cm., bottom 1.0 cm. thick	70		41	22
	55		34	14
Glass cased in close-fitting lead tube prolonged 50 cm. toward bulb	–	52[1]	25	12 cm.

Media pervious with difficulty eliminate the secondary radiation entering the broadsides and to close the end towards the bulb is to eliminate nearly all the rays; but if this is open, the number of nuclei instantly generated decreases much more slowly than the first power of distance. The fact that to the wooden fog chamber the medium within a sphere of at least 6 meters in radius remains almost equally energized throughout remains a result of importance.

9. *Nucleation Due to Gamma Rays.*—To what extent nucleation is producible by gamma rays may be tested by radium enclosed in a thick chamber of lead. The results are strikingly confirmatory. For instance in case of radium (10,000×) enclosed in a hermetically sealed aluminum tube and placed outside, but close to the end of the fog chamber (bottom nearly 1 cm. thick, walls .3 cm. thick), the data were

Radium in sealed aluminum	$10^{-3}N=27$	Transmission 100 per cent.
Radium in lead tube .5 cm. thick	23	85 per cent.
Radium in lead tube 1.0 cm. thick	18	69 per cent.

The nuclei are thus very largely due to this extremely penetrating radiation. By using lead tubes, capped and not capped, 30 cm. and 60 cm. long and placed parallel to the end of fog chamber, no evidence of secondary radiation was discernable, all the effective radiation passing through the lead walls. Hence while the gamma rays of radium contribute but a few percent. of the ionization of the air, they produce nearly the whole of the nucleation.

10. *Distance Effect in Case of Radium.*—In comparison with the abundant nucleation after the penetration specified, the decrease of nucleation observed when the tube is at different distances, D, from the fog chamber is remarkably large. For example

$D=$	0	10	30	50	100	200	cm.
$N\times 10^{-3}=$	30	13	8	5	3	2	

If measurement be made from the line of sight (10 cm. from end of fog chamber) the nucleation decreases less rapidly than the first power of distance. Hence whereas the distance effect in case of X-rays is small, it is very large in radium. On the other hand, rays from radium show remarkable nucleating power after penetrating many centimeters of lead, whereas the nucleating power of the X-rays after such penetration is relatively negligible.

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[1] Through .14 cm. of lead $10^{-3}N=3$; through .05 cm. of iron $10^{-3}N=44$.

11. *Axial Nucleation Within the Fog Chamber.*— Finally, when the rays have once entered the fog chamber, the nucleation along the axis seems nearly uniform. Measurements are difficult, but while the nucleation decreases to nearly one-fourth when the radium is placed on the outside of the fog chamber, 40 cm. (axially) from the end, the coronas along 40 cm. within the fog chamber are nearly of the same aperture for any given position of the radium tube.

OPTICAL ROTATION BY A QUARTZ PRISM.[1]

BY H. M. REESE.

IN this paper, which is merely a preliminary note, the author has investigated mathematically the form of the diffraction pattern which would result from a rectangular opening if the beam of light were polarized, not all in the same azimuth, but in an azimuth which varies uniformly from one side of the beam to the other. Such a beam is furnished by a quartz prism cut so that the optic axis is parallel to the base of the prism and normal to its refracting edge if the incident light is plane polarized. The theory indicates two principal maxima instead of one, the general form of the pattern depending upon the width of the beam as compared to the rotating power of the quartz. The phase-relations show that the two principal maxima are circularly polarized in opposite senses. This shows that Fresnel's observation that plane-polarized light is resolved into two circularly polarized components can be explained purely on the basis of diffraction.

POLARIZATION OF STANDARD CELLS.[1]

BY R. R. RAMSEY.

MY purpose in performing the experiments described below was to determine the character of the polarization of cells, containing mercurous sulphate, when they are connected to a battery. The cells were made according to the usual formula for cadmium cells of the H form. Connections were made as in Fig. 1. *S* is the cell under investigation. *E* is a battery of five cells. *A* is milliammeter. *C* is a commutator. *R* is a resistance box. *PP'* is a potentiometer. *B* is the potentiometer battery. *G* is a galvanometer in the potentiometer circuit. *R'* is a resistance box. *K* is a contact key by means of which any one of six cells (one of which was never used except as a standard) could be thrown into the potentiometer circuit, *C* being open. By opening *K* and closing *C* current could be forced through the cell under investigation in the direct or reversed direction. By varying the resistance, *R*, the approximate resistance of the cell could be determined. From the current, the resistances in the circuit, and the difference of potential at the terminal of the battery, *E*, the e.m.f. of the cell, *S*, could be determined. In the first runs, the change in the potential of the cells is shown by plotting the current as ordinates and time as abscissas. In cells the diameter of whose mercury electrode is 1 cm. with a current of about four milliamperes, the initial current is proportional to the total e.m.f. in the circuit, curve I, Fig. 2. The current gradually decreases and reaches a steady value in about ten minutes. This steady value being proportional to the e.m.f. of the battery *E*. After remaining constant from two to four hours, say, the current rapidly decreases to an unsteady value near zero. If the current is broken at any time after the first decrease, the potentiometer shows its e.m.f. to be a few hundredths volts. The The e.m.f. gradually increases and after short runs the cell may regain

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

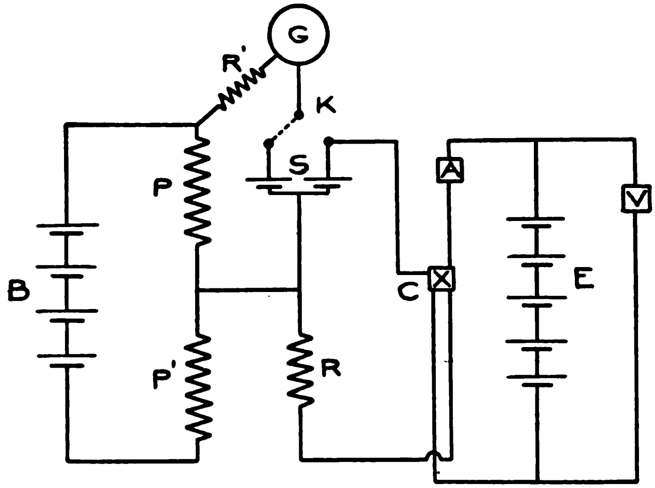

Fig. 1.

its original e.m.f. to within a few thousandths of a volt. After very extended runs the cells recover very slowly, in one case from 0.017 to 0.084 volts in two weeks. If the current is reversed after the cell has been run down, the current increases to a maximum in about ten minutes and then rapidly decreases to an unsteady value near zero, Curve 3 and 5, Fig. 2. Potentiometer readings after a run show the e.m.f. to be near the normal value. A double *H* cell was made with three electrodes, two of mercury and one of cadmium. Connections were made with the cadmium and one of the mercury electrodes and the cell allowed to run down. The potentiometer shows the e.m.f. between the cadmium and second electrode to be normal, showing the polarization to be at the mercury terminal.

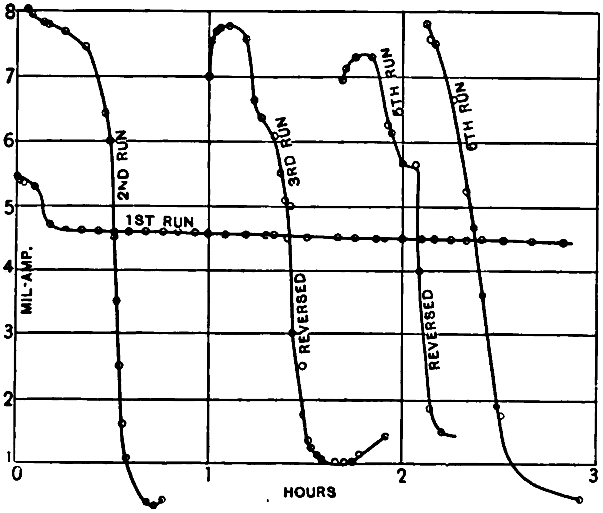

Fig. 2.

ON THE MEASUREMENT OF CURRENT BY A QUADRANT ELECTROMETER.[1]

BY O. M. STEWART.

CASE investigated is that where the current flowing into a conductor connected to one pair of quadrants is measured by determining the velocity of the needle. This is the usual method in radioactivity work.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

Two cases are considered: First, that where the change in capacity of the electrometer due to the motion of the needle does not appreciably affect the capacity of the apparatus. And second, the more general case, where the capacity is treated as a variable.

It is shown that after the needle has reached uniform motion the current is proportional to the angular velocity of the needle. A simple method is given for finding the time it requires for the needle to reach this uniform speed. When the capacity is constant the time for the needle to acquire a velocity within say 2 per cent. of the final velocity is the same as the time required for the needle to return when grounded to a vibration having an amplitude of 2 per cent. of the original steady deflection.

In the second case it is shown that after the velocity has become constant, the effective capacity becomes constant and has then the value given by Professor J. J. Thomson.[1] The ratio of the effective capacity to the capacity when the needle does not move can be obtained from the ratio of the deflection when the quadrants are connected to a certain potential to the deflection when the quadrants had only been connected a very short time.

It is found that the maximum sensibility for current work does not coincide with the maximum sensibility for steady deflections. When the potential of the needle is changed until the effective capacity is twice the capacity when at zero and not allowed to move, the electrometer will be the most sensitive. This however is true only when the potential of the needle is below the potential giving maximum sensibility for ordinary deflections. It is worth consideration when the capacity connected to the electrometer is small compared to that of the electrometer itself.

The equations deduced for the motion of the needle show that the deflection reached in a definite time after the ground is broken is in all cases proportional to the current. It is not necessary in this method to wait until the velocity has become uniform. It is however necessary to eliminate the disturbance sometimes caused by the breaking of the ground connection.

Surface Tension by the Method of Liquid Jets.[2]

By Floyd R. Watson.

When a liquid issues horizontally from a small, nearly circular orifice in a thin wall of a vessel, the stream formed assumes a definite shape, the boundaries of which are fixed. In the case of an elliptical orifice the shape of the jet may be likened roughly to that of a link chain, the links—crests—being first horizontal, then vertical, giving the appearance of standing waves on the stream. Fig. 1 is a photograph of such a stream.

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[1] Philosophical Magazine.

[2] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

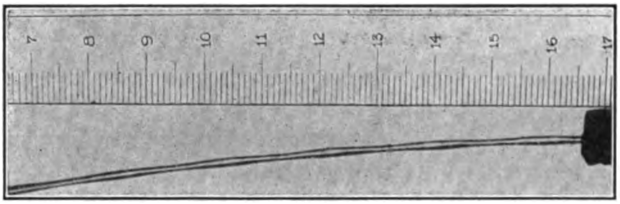

Fig. 1.

The complete explanation of the properties of the jet was given by Rayleigh[1] in 1879. The equation deduced for this case is as follows[2]:

$$p = \pi^{\frac{3}{4}} A^{-\frac{3}{4}} \sqrt{\frac{T}{\rho}} \sqrt{n^3 - n}$$

where $p/2\pi$ is the frequency of the motion; A is the mean cross-section of the jet; T the surface tension; ρ the density; and n the mode of vibration, being equal to unity for a circular jet, two for a jet from an elliptical orifice, three for a jet from a triangular orifice, etc. As the frequency $p/2\pi$ equals the velocity divided by the wave-length v/λ, the equation may be written,

$$\lambda = \frac{2\pi^{\frac{1}{4}} v A^{\frac{3}{4}}}{\sqrt{n^3 - n}} \sqrt{\frac{\rho}{T}}$$

from which the surface tension is expressed as

$$T = \frac{4\pi^{\frac{1}{2}} v^2 A^{\frac{3}{2}} \rho}{(n^3 - n)\lambda^2}.$$

The tension may then be calculated when values are found for λ, v, and A.

The method of measurement used was suggested by Rayleigh[1] though he did not use this formula for the absolute determination of surface tension. The apparatus used is shown in Fig. 2. A glass bulb D which can be raised or lowered, contains the liquid whose tension is to be determined. A rubber tube fastened to the base of this bulb allows the liquid to pass to a horizontal tube B and thence to the air through an elliptical orfice about 1 mm. in diameter. A transparent glass scale C is attached to B in a vertical plane that includes the axis of the jet.

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[1] Proc. Roy. Soc., 29, 71, also Theory of Sound, Vol. 2, §§ 357, 358.

[2] Theory of Sound, Vol. 2, § 358, equation 1.

[3] Proc. Roy. Soc., 47, 281.

The velocity v is calculated from the relation $v = \sqrt{2gh}$, h being the vertical distance from the level of the liquid in D to the level of the orifice in B. A is found from the relation $m = vAt\rho$, where m is the mass of fluid that passes through the orifice in the time t. The value of λ is obtained by measuring the distance between two adjacent crests on the jet. This measurement is subject to error in that the wave-lengths are small — from 1½ to 3 cm. — and that it is difficult to estimate the position of the center of each crest. Further, as λ depends on the pressure head h which is constantly decreasing, an element of haste is introduced.

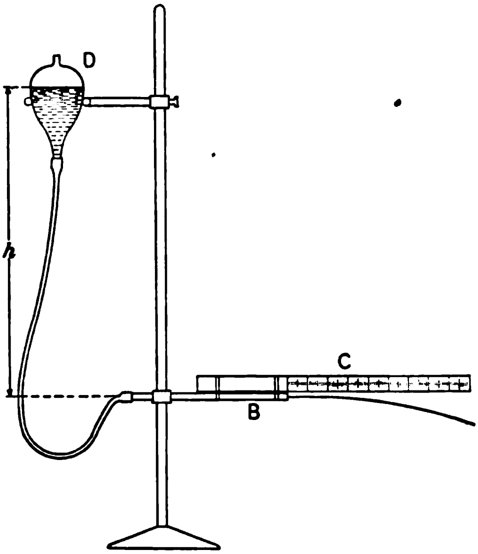

Fig. 2.

Special means were taken to lessen these chances for error. The jet was placed in front of a lecture lantern so that its shadow was thrown on the screen, thus magnifying the distance λ about 20 times. λ was then measured with a beam compass and read off on the scale C which was also thrown on the screen and magnified in the same proportion as the jet. Fig. 1 is copied from a photograph of the screen when the shadow of a jet of water was thrown on it. The time of exposure was about 20 seconds, and the head h diminished about 3 cm.

Measurements were taken by the above method for water, water contaminated with oil, mercury, and mercury wet with water. The following table gives results :

Date.	Liquid.	λ	h	m	t	Temp.	T
Mar.23	water.	$3\lambda=5.3$ cm.	39 cm.	98.8 gms.	20 sec.	21 C	69.1
" 29	water.	$3\lambda=5.53$ "	44.6 "	133.1 "	25.2 "	23.5	70.5
" 29	water and oil.	$3\lambda=2.48$ "				"	39.8
" 29	water repeated.	$3\lambda=5.46$ "	42.0 "	141.2 "	27.2 "	"	71.3
" 27	mercury.	$\lambda=1.5$ "	16.1 "	852 "	20 "	22 C	527
" 27	mercury wet with water.	$\lambda=1.5$ "	16.5 "			"	527?
April 3	mercury.	$2\lambda=3.44$ "	19.0 "	1006 "	21 "	21.1	495
" 3	mercury wet with water.	$2\lambda=3.41$ "	18.3 "			"	484.8

The tensions found for water are less than the values found by other methods, the accepted value being about 73 dynes per cm. at 23° C. The effect of oil on water is interesting. Oil was forced into the aperture from which the jet escaped, then a water jet was set up which passed through this layer of oil. The tension dropped from 70.5 dynes to 39.8 dynes; then as the oil became washed out, the jet changed its form back to the water jet and the tension rose to its former value. From this measurement it seems that a newly-formed water surface when contaminated slightly with oil does not drop immediately in tension. This is in accordance with a result found by Rayleigh[1] where a freshly formed surface of soap solution had nearly the same tension as pure water.

The results found for mercury are not so satisfactory as the water tensions; the values varying from 527 to 495 dynes per cm. for different days. Yet both of these values are good ones compared with previous work done by the writer,[2] where the highest tension found was 510 dynes per cm. Good results should be expected by this method for the surfaces are not exposed long enough to the air to cause the tension to drop.

Tensions for mercury wet with water do not show an appreciable variation from the tensions of mercury supposedly not wet. Two conclusions seem probable in this connection; first, that the mercury was wet in *both* measurements, and second, that a fresh surface of wet mercury has nearly the same tension as dry mercury. It is not improbable that the mercury was wet all the time, for the reason that it was cleaned with concentrated H_2SO_4 and pasty mercurous sulphate.[3]

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[1] Proc. Roy. Soc., 47, 281.

[2] Phys. Rev., 12, 257.

[3] Phys. Rev., 12, 264.

COMPARISON OF THE MUTUAL INDUCTANCE OF A PAIR OF COILS WITH THE SELF INDUCTANCE OF ONE OF THEM.[1]

By Robert T. Herdegen.

MAXWELL'S method[2] is modified so as to permit the use of the differential transformer as a measuring instrument.[3] The balance condition being equality of amplitude and phase of the two currents in the differential transformer simplifies the expression for the ratio of L to M. The sharpness of the balance makes it possible to determine this ratio to an accuracy of one-tenth per cent. for a single observation.

THE RADIUS OF MOLECULAR ATTRACTION.[1]

By C. W. Chamberlain.

IT has been suggested that it would be impossible for a liquid film to exist, the thickness of part of which is less than twice the radius of molecular attraction. Quinke reached the conclusion that the radius of molecular attraction is approximately equal to $5(10)^{-6}$ cm. Johonott found that the minimum thickness which a soap film can attain is $6(10)^{-7}$ cm., while the limiting thickness attained by the first black is $1.2(10)^{-6}$ cm.

If Johonott's measurement of the limiting thickness of a liquid film can be taken as a determination of the radius of molecular attraction, the discrepancy between this value and that of Quinke remains to be explained.

A silver wedge was formed upon a plate of optical glass and Quinke's method employed for finding the point at which the thickness of the silver was equal to the radius of molecular attraction. Quinke estimated this thickness by its color. An attempt was made to measure the thickness by means of a Michelson interferometer. If Quinke's value $5(10)^{-6}$ cm. is correct, assuming the index of refraction of silver to be .25, the shift in the interferometer ought to be .15 of a fringe. The shifting of the fringe was in every case less than this amount.

A multiple reflection or compound interferometer was devised, suitable for making rapid and accurate measurements of thin wedges of small area. Light incident on a plane parallel plate provided with a thin film of silver was reflected and refracted to two mirrors placed at angles of 67½ degrees to the plane parallel plate. The light was reflected from these two mirrors in paths parallel to each other to a third mirror and then to a fourth. The third and fourth mirror made a slight angle with each other and the parallel rays were thus reflected many times between them and finally returned along their entering paths where they were made to recombine and interfere. By changing the angle between the third and fourth mirror by means of a single adjusting screw the instrument could be compounded from one to twenty times. It possessed the advantage of showing interference fringes of several powers in the field of view at the same time. The observer could quickly and conveniently select that power best suited to the measurement of the magnitude under investigation.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, April 22, 1905.

[2] El. and Mag., Vol. II., p. 365.

[3] A. Trowbridge, Phys. Rev., CVII., February, 1905.

As it was desirable to test the accuracy of Quinke's determination and as Kundt's value for the index of refraction of silver is somewhat in doubt, the silver wedges were changed into silver iodide before their thickness was measured.

The work has progressed far enough to indicate that Quinke's value for the radius of molecular attraction is at least twice too large.

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THE PHYSICAL REVIEW.

THERMO-ELECTRIC DETERMINATION OF TEMPERATURES BETWEEN 0° AND 200° CENTIGRADE.

By A. de Forest Palmer, Jr.

THE thermo-electric thermometer has been developed, for the most part, in connection with the measurement of very high or very low temperatures and neither the instruments nor the reduction formulæ in common use are available for accurate work in the interval between 0° and 200° C. The apparatus and method, described in some detail below, were, accordingly, developed for the purpose of determining the precision attainable in this interval with suitably chosen thermo-elements. At the outset, the well-known thermo-electric properties of constantin suggested the adoption of the iron constantin element, but, at that time, constantin wire of suitable size could not be obtained, without considerable delay due to the necessity of importation. To save time, wire supplied by the Driver-Harris Wire Co., of Harrison, N. J., under the trade name "Advance," was tried. Analysis of a sample of this wire showed that it contained approximately 55 per cent. copper, 44.4 per cent. nickel and 0.6 per cent. iron. A preliminary calibration of an element, composed of advance wire in conjunction with commercial soft iron wire, by comparison with an uncorrected mercury thermometer showed a nearly linear relation between thermo-electromotive force and temperature when the cold junctions were kept at a constant temperature. The mean electromotive force per degree Centigrade in the range from 0° to 100° C. was found to be approximately fifty micro-volts. These results agree so closely with the known composition and properties of constantin that it seemed inexpedient to incur the delay of importation and the following observations were, accordingly, made with iron-advance thermo-elements.

OUTLINE OF THE METHOD.

The thermo-elements were connected to a potentiometer by copper wires. The copper-iron and copper-advance junctions were kept constantly at 0° C. in melting ice, while the iron-advance junction was immersed in various constant temperature baths, and the resultant electromotive forces were measured in the usual manner by comparison with a Clark cell. During the preliminary tests of the apparatus considerable uncertainty in its indications was produced by residual thermo-electric effects, *i. e.*, by the electromotive forces generated in the various parts of the potentiometer and at other junctions than those under test. These residual effects were due largely to lack of uniformity in the temperature of the various parts of the potentiometer system; they varied continually, but never abruptly, in magnitude and sign and their resultant magnitude sometimes amounted to ten micro-volts. Since it was impracticable to keep the whole apparatus at a perfectly uniform and constant temperature an auxiliary potentiometer, described below, was introduced in such a manner as to balance the residual effects without, at the same time, impeding the action of the electromotive force due to the element tested. When this device was properly adjusted the uncertainty of a single determination rarely exceeded one micro-volt.

HOT JUNCTION TEMPERATURES.

The iron-advance junction was maintained successively at the transition temperature of sodic sulphate ($Na_2SO_4 + 10H_2O$) and the boiling points of benzene (C_6H_6), distilled water, chloro-benzene (C_6H_5Cl), and aniline (C_6H_7N). The temperature corresponding to each boiling point was calculated from the corrected height of the barometer at the time of observation. Somewhat greater accuracy in fixing these points might have been attained by the judicious use of well constructed and carefully calibrated mercury thermometers, but, as such instruments were not available, reliance was necessarily placed on published determinations of the boiling constants of the various liquids.

Sodic sulphate, marked C.P., was obtained from Eimer and Amend and recrystallized until further continuance of the process produced no change in the transition temperature. Two successive crystallizations usually proved sufficient and, when the heating bath was kept between 33° and 34°C., various samples of the salt exhibited the same transition temperature, within the errors of observation; moreover this temperature remained constant, within the same limits, for long periods of time. As a datum in exact thermometry this point is comparable with the ice point in convenience and accuracy of maintenance and is much superior to any of the boiling points since it is independent of fluctuations in atmospheric pressure. A series of very accurate determinations by Richards and Wells[1] gives 32°.383, hydrogen thermometer scale, as the exact temperature at which transition takes place.

All of the organic liquids, enumerated above, were Kahlbaum products. They were carefully fractionated, in the chemical laboratory of Brown University, until they maintained constant boiling points, and the sample of benzene had stood in contact with sodium wire nearly a year for the purpose of freeing it from water. The boiling points of these liquids have been determined by several observers and the following values, referred to the air thermometer scale, have been adopted as the most trustworthy.

Liquid.	Boiling Point.
Benzene......................	$80^\circ.19 + .0455\,(H - 760)$
Chloro-benzene............	$131^\circ.85 + .049\,(H - 760)$
Aniline..................	$184^\circ.13 + .051\,(H - 760)$

The first of these values was taken from a paper by Holman and Gleason[2] and the second was calculated from the air thermometer observations of Ramsay and Young,[3] using .00367 for the coefficient of expansion of air. The normal boiling point of aniline is due to Callendar and Griffiths[4] and the pressure coefficient .051 to Ramsay and Young.[5] The temperature of the steam from water boiling under observed atmospheric conditions was taken from Landolt and Börnstein's "Physikalisch-Chemische Tabellen."

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[1] T. W. Richards and R. C. Wells, Proc. Am. Acad., Vol. 38, p. 431, Dec., 1902.

[2] S. W. Holman and W. H. Gleason, Proc. Am. Acad., Vol. 15, p. 237, 1888.

[3] William Ramsay and Sidney Young, Trans. Chem. Soc., Vol. 47, p. 645, 1885.

[4] H. L. Callendar and E. H. Griffiths, Chem. News, Vol. 63, p. 1, January 2, 1891.

[5] William Ramsay and Sidney Young, l. c., p. 655.

APPARATUS.

The construction of the thermo-elements is exhibited in Figs. 1 and 2. *Ad* is a No. 30 B.S. advance wire and *Fe* is a commercial soft iron wire of nearly the same diameter. These wires pass through openings in the cork *K*, Fig. 2; *Fe* inside and *Ad* outside of a glass tube *L* about one millimeter internal diameter, three millimeters external diameter, and twenty centimeters long. They are soldered together at *G* to form the hot junction. The cold junctions *J*, *J'*, Fig. 1, are constructed in essentially the same manner. Both *Fe* and *Ad* pass inside of glass tubes *T*, *T'*, of the same dimensions as *L*, Fig. 2, while the copper wires *Cu*, *Cu*, leadng to the potentiometer, are outside of the tubes. The length of the wires between *C*, Fig. 1, and *K*, Fig. 2, is about one meter. Both of these wires and also the copper wires *Cu*, *Cu* are insulated by passing through small rubber tubes and all of the wires and tubes are held firmly in place in the corks *C* and *K* by sealing wax caps *W*, *Y* so that the element can be easily removed from one heating bath to another. Three elements, constructed from different portions of the same samples of wire, were tested. The iron-advance junctions were entirely independent of one another but all of the copper-iron and copper-advance junctions were brought together in the tube *U* of the cooling apparatus, Fig. 1, for the purpose of keeping them at a uniform temperature. For the sake of clearness only one pair of junctions *J*, *J'* is delineated in Fig. 1, but in practise the three pairs were held firmly together by the cork *C* and a rubber band around the lower ends of the tubes *T*.

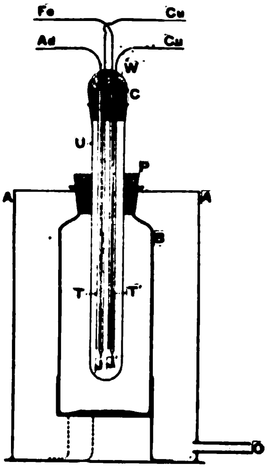

Fig. 1.

The cooling chamber, Fig. 1, consists of a wide-neck glass bottle *B*, about 600 c.c. capacity, centrally supported in a tin plate tank

AA, 22 cm. high and 15 cm. diameter. A strong test tube *U*, filled to about one third its capacity with paraffin oil, is supported, with about two thirds its length in the bottle *B*, by the cork *P* and serves as a bath for the cold junctions *J*, *J'*. The tank *AA* was placed inside of a large wooden box covered with asbestus to shield it from direct radiation from the heating apparatus at the hot junction. Clear pond ice, free from specks and air bubbles, was crushed to about the size of large chestnuts and carefully washed with distilled water, while contained in a glass funnel to allow free drainage. About two thirds of the anular space between *U* and *B* was filled with ice thus prepared and the remaining space was filled with distilled water. The space between *A* and *B* was filled with ordinary crushed ice. After standing twenty or thirty minutes, with occasional agitation of the ice and water in *B* by means of the tube *U*, which was slightly raised from its normal position for the purpose, the temperature of the oil in *U* became uniform and remained perfectly constant, within the limit of sensitiveness of the thermo-elements, as long as the apparatus was in use; ten or twelve hours on some occasions. The drainage tube *O* was normally closed by a rubber tube and pinch cock but it was occasionally opened to drain off water, due to melting of the ice in *A*, after which the space between *A* and *B* was again filled up with crushed ice. When the iron-advance junction was immersed in a similarly constructed bath, charged with various samples of pond ice prepared as described above, the resultant electromotive force of the system was invariably too small to be detected with the galvanometer used in these experiments, although it easily showed a difference of potential of one tenth of a micro-volt between its terminals. It was, therefore, concluded that the temperature of the bath *B* represented the true melting point of ice within the limit attainable by the present method.

The sodic sulphate bath is illustrated in Fig. 2. *DD* is a glass beaker, 18 cm. high and 10 cm. diameter, nearly filled with water and provided with a german silver heating coil *HH*. The test tube *E*, 20 cm. long and 3.5 cm. diameter, is supported axially in the beaker by a clamp stand not shown in the figure. *F* and *S* are smaller test tubes supported concentrically with *E* by the corks *N* and *M.* *S* contains paraffin oil, that serves as a bath for the iron-advance junction, and *F* contains sodic sulphate, prepared as described above. Sufficient salt was introduced to keep *F* filled nearly as high as the surface of the water in *DD.* The anular air space between *E* and *F* serves to render the interchange of heat between the two tubes more uniform and aids materially in maintaining a constant temperature. A mercury thermometer was immersed in the water in the beaker and the temperature quickly raised to about 33° C. with a Bunsen burner. The coil *HH* was then connected to a storage battery through an ammeter and rheostat and the current strength was adjusted so that the temperature of the bath remained nearly constant. The tube *F* was cautiously heated, over a Bunsen flame, until the sodic sulphate began to melt; it was then placed in the water bath, as indicated in Fig. 2, and the salt thoroughly stirred, with the tube *S*, until equilibrium was established and the temperature remained constant. The essential features of this apparatus and method of manipulation are the same as those adopted by Richards and Wells[6] in their determination of the transition temperature.

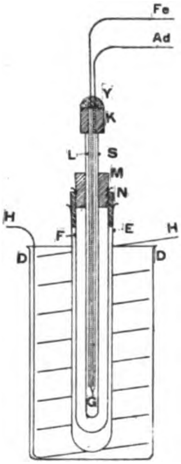

Fig. 2.

Vapor jacketed hypsometers were employed with benzene and water. These instruments were of the well known type, adapted to the determination of the boiling points of accurate mercury thermometers in the vertical position, and were provided with tubular oil baths, similar to *S*, Fig. 2, in the place usually occupied by the thermometer. The instrument used with water was made of tin plate and held about one liter of water. It was not provided with a condenser and hence volatile impurities in the water would produce a gradual change in the boiling point. Since the observations give no evidence of such a change, it was assumed that the distilled water employed was free from such impurities. A sheet copper hypsometer, provided with an inverted condenser, was used with benzene and the condenser was occasionally turned over to test the constancy of the boiling point. Both of these instruments were jacketed on the outside with felt packing and asbestus and contained a quantity of sharp-pointed bits of copper wire to insure quiet boiling and prevent super-heating.

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[6] T. W. Richards and R. C. Wells, l. c.

Chloro-benzene and aniline were boiled in the apparatus illustrated in Fig. 3, some features of which are due to Barus.[7] *T* is a glass boiling tube, 36 cm. long and 4.5 cm. internal diameter, surrounded by a plaster of paris muffle *MM*, 20 cm. long and 15 cm. diameter. The muffle was protected by the tin plate can in which it was cast and, together with the other parts of the apparatus, was supported by a clamp stand not shown in the figure. The top of the boiling tube was closed by a cork *P* that supported a tubular oil bath *S* and an inverted condenser *C*. The muffle and the vapor in the upper part of *T* were protected from the direct radiation from the ring burner *B* by an asbestus diaphragm *A* and the lower end of *T* was surrounded by fine brass gauze *G* to insure uniform heating. A number of short capillary tubes, closed at the upper end and supported vertically in the liquid, caused the ebullition to progress regularly and quietly. The surface of the liquid was never allowed to fall below the diaphragm *A* and the burner was so adjusted that the condensation line in the condenser *C* remained at an approximately constant height, 10 to 15 cm., above the cork *P*. Under these conditions the temperature of the vapor remained perfectly constant so far as could be detected by the thermo-elements. During the course of the experiment the constancy of the boiling point was tested by inverting the condenser and allowing the liquid to distill over. The purity of the liquids is attested by the fact that this process never produced a definitely observable change in the temperature of the vapor, although more than half the volume of liquid was allowed to pass over in some cases.

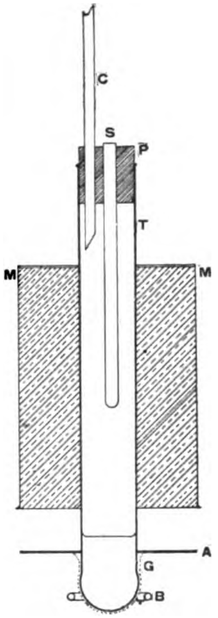

Fig. 3.

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[7] Carl Barus, Bulletin No. 54, United States Geological Survey, 1889.

Fig. 4 is a schematic diagram of the potentiometer system and connections. The resistances R_1, R, R', and the slide wires A–A' and E–E' constitute the primary potentiometer and are connected in series with a single storage cell B through the double pole switch S. The variable high resistance R_2 and the slide wire F–F', connected in series with a single dry cell B' through the reversing key D, constitute the auxiliary potentiometer, used to balance the residual thermo-electric effects. The thermo-element T is connected to the primary potentiometer, through the three way double pole switch W, the double pole double throw switch P, the galvanometer G, and the length F–M of the auxiliary potentiometer wire, as indicated by the full lines in the diagram and its electromotive force is balanced against the fall of potential along HA and the resistance

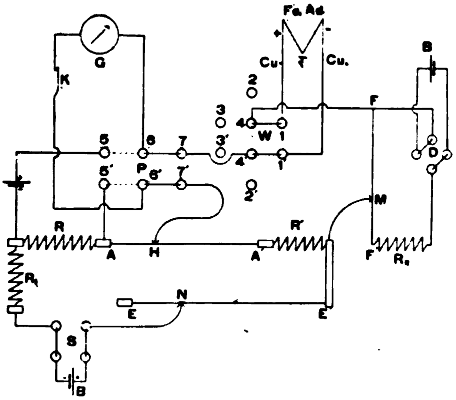

Fig. 4

R'. For the sake of clearness only one of the elements is represented in the drawing. The other two are connected to the points 2, 2′ and 3, 3′ respectively and the interchange of elements is easily effected by moving the connection bars 4–1 and 4′–1′ of the switch W. When the switch P is thrown to the position indicated by the dotted lines 5–6 and 5′–6′ the Clark cell C is connected to the primary potentiometer, through the galvanometer, and its electromotive force is balanced against the fall of potential through a fixed resistance R of about 2,000 ohms. The slide wire A–A' was carefully calibrated and the resistances R and R' were accurately determined in terms of its mean resistance per unit length. The contact H was moved by an endless wire belt actuated by a milled head, situated at the end of the slide wire, and its position was determined by a vernier reading directly to one tenth of a millimeter.

Observations.

With the switch P, Fig. 4, thrown to the position 5–6, 5′–6′ and the switch S closed, the resistance R_1 and the sliding contact N were so adjusted that the galvanometer showed no deflection when the key K was closed. P was then thrown to 6–7, 6′–7′, R' and R_1 changed reciprocally, and H moved along the wire until balance was again produced. The connection bar 4–1 was then moved to the position indicated by the dotted line 4–4′, S was opened, and the residual electromotive forces were balanced by properly adjusting the commutator D, the resistance R_2, and the sliding contact M. These operations were repeated, in the above order, until exact balance was observed in each of the three cases without changing the potentiometer adjustments. Usually two repetitions sufficed for this purpose and, as the various switches could be worked rapidly, the necessary operations caused very little loss of time and inconvenience.

When these adjustments have been made it is obvious that the resultant electromotive force (V), in micro-volts, of the element connected to the potentiometer is given by the expression

$$V = (R' + x)\frac{E}{R} \times 10^6 \tag{1}$$

where E is the electromotive force of the Clark cell at the time of the observation, R and R' are resistances, designated in Fig. 4, expressed in terms of the resistance of one centimeter of the slide wire, and x is the corrected length of the wire between A' and H. The electromotive force of the Clark cell used in these experiments was given by the formula

$$E = 1.438 - .001(t - 17) \tag{2}$$

where t is the temperature of the cell, and the resistance R was equivalent to 148,870 cm. of the slide wire. Substituting these values in (1) gives

$$V = (R' + x)\,[9.659 - .007\,(t - 17)] \tag{3}$$

Hence, a change of one millimeter in x is equivalent to a change of a little less than one micro-volt in V and as the contact H can be easily set and read to one tenth of a millimeter the limit of sensitiveness of the apparatus is about one tenth of a micro-volt.

During all of the observations the copper-iron and copper-advance junctions were maintained at 0° C. in the bath illustrated in Fig. 1 and, before each observation, the mixture of ice and water in the bottle B was thoroughly stirred. The first series of measurements was made with the iron-advance junction immersed in the sodic sulphate bath, thus producing 32°.383 difference in temperature between the hot and cold junctions. Before each observation the salt in the tube F, Fig. 2, was thoroughly stirred and immediately after balancing the potentiometer the temperatures of the Clark cell and the water bath D were noted. The three elements were tested in succession; about five independent observations being taken with each element while the other two were at room temperature. Two series of observations were made in this manner before the elements were raised to a higher temperature and two similar series were taken after all of the observations at other temperatures had been completed. The average deviation of a single observation from the mean electromotive force of the corresponding element was 0.5 of a microvolt; an amount that corresponds to a change of about one hundredth of a degree in the temperature of the element. Nearly three months elapsed between the first two series of observations and the last two. During this interval the elements were subjected to frequent abrupt changes in temperature sometimes amounting to nearly 200° C. The mean electromotive force derived from the first two series differs from that derived from the last two by only three tenths of a micro-volt. Hence, the temperature baths can be reproduced within somewhat less than one one hundredth of a degree and the thermo-electric properties of the elements are permanent within the errors of observation.

Essentially the same procedure was adopted when testing the elements in the other temperature baths. Care was taken to keep the liquids boiling at a uniform rate, as indicated by the height of the condensation level in the condenser, and after each observation the height and temperature of the barometer were accurately observed. Owing to fluctuations in the atmospheric pressure, and consequently in the temperature of the baths, the individual observations corresponding to the several boiling points do not agree so closely among themselves as do the observations at the transition temperature of sodic sulphate but in all cases the electromotive force of the element followed the changes in temperature of the baths with satisfactory regularity and no detectable change in boiling point due to distillation was observed.

The observations were reduced with the aid of a table, showing the corresponding values of t and log $[9{,}659 - .007\ (t - 17)]$, and the mean results, corresponding to the various temperature intervals, are brought together in Table I., where the data relative to each element are entered in a separate section. The first column gives the number of individual observations from which the mean electromotive force of the element (V_T) was calculated and the second column gives the values of V_T, in micro-volts, thus obtained. The third and fourth columns contain the mean corrected height of the barometer (H) and the mean temperature (T) of the iron-advance junction respectively.

TABLE I.

			Element No. 1. $V_{100} = 5{,}188.9$				
N	V_T	H	T	θ	T'	e	$e\%$
20	1,629.5		32.383	31.405	32.385	.0067	.021
23	4,131.4	761.76	80.270	79.618	80.265	.0091	.011
16	5,192.0	761.50	100.055	100.060	100.058	.0098	.010
28	6,916.8	760.20	131.86	133.30	131.81	.0478	.036
18	9,776.6	755.39	183.89	188.41	183.87	.0211	.011
			Element No. 2. $V_{100} = 5{,}190.2$				
22	1,629.9		32.383	31.403	32.383	.0115	.036
11	4,133.1	761.78	80.271	79.632	80.279	.0073	.009
16	5,193.2	761.33	100.048	100.058	100.056	.0217	.022
15	6,915.4	758.34	131.77	133.24	131.75	.0286	.022
13	9,785.6	756.85	183.97	188.54	183.99	.0191	.010
			Element No. 3. $V_{100} = 5{,}194.1$				
20	1,631.1		32.383	31.402	32.382	.0120	.037
11	4,135.2	761.73	80.269	79.614	80.261	.0089	.011
15	5,196.0	760.96	100.035	100.038	100.037	.0099	.010
15	6,919.2	758.08	131.76	133.21	131.72	.0414	.032
13	9,792.3	757.35	183.99	188.53	183.98	.0119	.006

Empirical Formulæ.

For the purpose of developing an empirical formula to express the relation between the observed electromotive force of the elements and the temperature of the junctions let

$$\theta = 100 \frac{V_T}{V_{100}} \qquad (4)$$

where V_T and V_{100} represent the electromotive forces generated when the iron-advance junction is maintained at the air thermometer temperatures $T°$ and 100° respectively and the copper-iron and copper-advance junctions are at the temperature of melting ice. The values of V_{100} given in Table I. were obtained by interpolation between the results of two series of observations at the boiling point of water, during one of which the atmospheric pressure was above normal and during the other below normal. θ may be called the thermo-electric temperature of the hot junction and since V_T is identically zero when T equals zero it is obvious that θ would be equal to T at all temperatures if V_T and T were connected by a linear relation. A large scale plot having V_T and T for coördinates shows scarcely perceptible deviation from a straight line but the calculated values of θ entered in the fifth column of Table I. show differences between T and θ varying from zero to about two per cent.

Since the difference $T - \theta$ changes sign as T passes through 0° and 100°, it was thought that the curve representing the relation between T and V_T might be a parabola, such as is usually found in thermo-electric measurements, but a reduction of the observations on this assumption led to larger discrepancies than those obtained with the linear equation. From an inspection of these results it was apparent that the true T, V_T curve was situated between a straight line passing through the points $T = 0$ and $T = 100$ and a parobola passing through the same two points. An equation of the third degree in the form

$$T - \theta = \theta(\theta - 100)(P\theta - Q) \qquad (5)$$

where P and Q are constants, was consequently tried and it was found to represent the observations with sufficient precision. This equation cannot be considered as a physical relation since it gives three values of θ, and consequently of V_T, corresponding to each value of T, whereas no such phenomena have been observed. It would, perhaps, be more rational to express $T - \theta$ as a function of T rather than of θ but, when tried, such a formula did not reproduce the observations so accurately as equation (5) and it greatly increased the labor of computation. Equation (5) has consequently been adopted as a purely empirical formula for the purpose of reducing the thermo-electric temperature θ to the air thermometer temperature T.

The constants P and Q were calculated from the mean values of θ and T corresponding to the transition temperature of sodic sulphate and the boiling point of aniline. The results thus obtained are given in Table II.

TABLE II.

Element.	$P \times 10^9$	$Q \times 10^7$
No. 1	1,163	4,905
No. 2	1,152	4,911
No. 3	1,165	4,920
Mean	1,160	4,912

The mean values of these constants were adopted and the accuracy of the reduction formula thus obtained was tested by reference to the actual observations. For this purpose equation (5) was put in the form

$$T = \theta + D \tag{6}$$

where

$$D = \theta(\theta - 100)(116\,\theta \times 10^{-8} - 4912 \times 10^{-7}) \tag{7}$$

and the curve represented by equation (7) was plotted on such a scale that values of D could be read off directly to 0°.01. To give an idea of the magnitude of the correction term D and the manner in which it depends on θ a few of the calculated values from which the above curve was plotted are given in Table III.

TABLE III.

θ	D	θ	D
0	0	100	0
25	0.867	125	−1.082
45	1.086	150	−2.379
75	0.758	175	−3.783

The individual observations were all reduced by equation (6) with the aid of the curve determined by (7) and the mean results thus obtained for each element, at each of the temperatures employed at the iron-advance junction, are entered under T' in Table I. In each case the actual probable error of a single observation and the percentage probable error of a single observation, entered under e and e per cent. respectively in Table I., were calculated in the usual manner from the residuals obtained by subtracting each of the values of T obtained by reduction from the corresponding value determined by the known temperature of the bath surrounding the hot junction.

Conclusion.

The results given in Table I. show conclusively that temperatures, in the interval from 0° to 200° C., can be determined, within one twenty-fifth of one per cent., with the iron-anvance thermo-element when the residual thermo-electric effects are suitably eliminated. Most of the necessary apparatus is to be found in every well-equipped physical laboratory and the remainder can be very easily constructed by any intelligent person. Although proper calibration requires determinations of the electromotive force corresponding to three independent temperature intervals, the necessary observations and reductions are not unduly tedious. The fixed temperatures adopted in this investigation, namely — the melting point of ice, the transition temperature of sodic sulphate, the boiling point of water and the boiling point of aniline — can be easily reproduced and maintained constant with sufficient precision. The materials required for this purpose are cheap and can be easily purified; aniline being the only substance likely to give trouble in this respect. The purity of the aniline can, however, be very easily tested by making observations during distillation, when slight impurities will produce a marked change in the boiling point.

When determining temperatures, after the element has been calibrated, the reductions can be facilitated by combining equations (1) and (4) and calculating θ directly to the formula

$$\theta = (R' + x)\frac{E}{RV_{100}} \times 10^8 \qquad (8)$$

with the aid of a table or curve showing the variation of the factor $E \times 10^8/RV_{100}$ with the temperature of the Clark cell. If a Weston cadmium element is used in place of the Clark cell the correction due to changes in its temperature will generally be negligible.

Under favorable conditions, temperatures, in the interval considered, can be somewhat more accurately determined with a properly constructed and carefully calibrated mercury thermometer than by the method herein described. But such an instrument requires very careful handling and gives reliable results only when suitable corrections are applied to its indications. In many cases it is very difficult if not impossible to determine these corrections with sufficient accuracy to obtain the highest precision in the measurement of temperature. In such cases the thermo-element is quite as accurate and often much more convenient than the mercury thermometer.

BROWN UNIVERSITY,
March, 1905.

THE VOWEL A^O (AS IN RAW), O (AS IN RODE), U (AS IN RUDE).

By Louis Bevier, Jr.

My researches into the nature of the vowels, conducted with the aid of the phonograph, and a recording instrument, have been published from time to time in the Physical Review, giving results for *a*, a^e, *ę*, i^e, and *i*. Since the publication of the last article, "The Vowel *i* (as in pique)," September, 1904, I have been taking records as opportunity allowed of the series a^o, *o*, *u*. The results reached are given below. A few preliminary words of explanation are needed.

The vowel a^o (as in raw) is a sound which in general is uniform in its pronunciation. As ordinarily pronounced, it is a single sound with no important shift of vocal position during its utterance. The results reached therefore by the analysis of a^o-curves are quite consistent, and accord precisely with what was to be anticipated. In general a^o is different from *a* (as in father) in a somewhat lower pitch both of the main resonance (1150:1100) and of the secondary resonance (700:650).[1]

Hence it is, that if *a* is recorded in the phonograph and the speed in reproduction is reduced the sound issuing is a clear and normal a^o. If the speed is quickened an a^o becomes *a* in reproduction, and if still further quickened the result is a species of a^e, but not a normal one. The reason for this is apparent by comparing the acoustic analysis of *a* and a^e.[2]

The vowel *o* is by no means so easy. In the first place, as spoken in America, it is usually a diphthong, beginning with an *o* and ending with an *u* glide. I have attempted to record and analyze the *o* sound simply, but in spite of great care the results with different voices do not show a close correspondence, a fact which greatly increases the difficulty of definite description, but which was to have been expected, since recent phonetic studies reveal the same differences and varieties of sound grouped together as *o*'s.

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[1] Physical Review, April, 1900.

[2] Cf. Physical Review, March, 1902.

With *u* another difficulty appears. Here there is often added (particularly in feminine utterance) a very high resonance, probably due to the closeness of the lips, which does not properly characterize the *u* sound. And this resonance is no more stationary for *u* than is the characteristic high resonance of *i* for that vowel,[1] but may vary within wide limits or be entirely wanting, without depriving the sound of a satisfactory *u* quality.

The most casual observation by ear, by instrumental registration of lip position, or by acoustic analysis, reveals the fact that *u* may be uttered with varying degrees of closeness and still be heard as *u*. Individuals even pronounce *u* in certain words, with an opening which brings it very near to a close *o*. It is therefore idle to expect that the curves will show as constant a character as the curves of sounds which are themselves more constant.

A comparison of the tables of analyses of *o* and *u* with those of a^e and *ę*, will show how much greater the agreement in detail is in the case of the "bright" vowels, than in the "dark" vowels which we are now studying.

Passing these generalities I present herewith tables of analyses for a^o, *o*, and *u*, as computed from phonograph curves. For explanation of the methods used, I refer the reader to the preceding articles of this series, particularly to the article of Professor Prentiss.[2]

In the table of a^o analyses, it will be observed that generally there is strong resonance at or near a frequency of 1,000 vibrations to the second. This is the chief and most characteristic region of resonance for the a^o timbre. On a fundamental of 128 vibrations to the second, VIII. (1,024) will be strong; at 256 it will be IV., at 320 III., etc.

Again there is a marked secondary region of resonance culminating at about 640 to the second. Taking the same chord-tones, we shall find that on a fundamental of 128 to the second V. will be strongly reinforced, and on a fundamental of 320 II. Comparing this result with the analyses of *a*, a^o is seen to be a low-pitched *a*.

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[1] Cf. PHYSICAL REVIEW, November, 1902.

[2] PHYSICAL REVIEW, November, 1902.

One further characteristic must be noted. In the series a-a^e-*ę*-i^e-i, there is seen to be a generally diminishing amplitude in the curves. Thus, save where the fundamental or chord-tone is strongly reinforced, the traces for a^e has less amplitude thus *a*, and so on till for *i* the trace does not generally travel far on either side of a median straight line. A^o on the other hand gives a trace of great amplitude, the greatest of any of the vowels studied except *u*. This is plain for the series *a*, a^e, *ę*, i^e, *i* by inspection of the sample curves shown.

The reason *u* shows so large an amplitude is not because its resonance is loudest, but because it is concentrated chiefly in the lowest frequencies, in the chord-tone or first upper partial, where great amplitude does not involve great energy. In the experimental work no effort was made to have the vowels sung with uniform loudness, hence the above comparison is merely a rough and ready test of average.

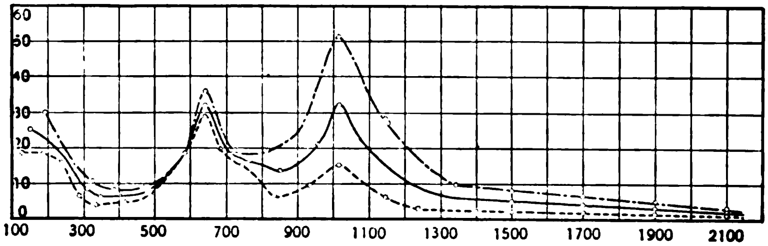

Fig. 1. A^o Resonance Curve.

The analyses of *u*, which for convenience I discuss next, show some interesting facts. This vowel is to be described acoustically with negative rather than with positive characteristics. The mouth cavity in the normal *u*-position seems to have no marked resonance higher than about 210 vibrations to the second. In low tones of men's voices, this may be heard as a strong reinforcement of II. *cf.* the first two analyses given in the tables, voices one and four at 113. Obviously however as the chord-tone rises, this resonance will shift from II. to I.

Where the chord-tone lies above, say, 250 vibrations to the second, the table shows great inconsistencies. This is due in part to inconsistencies of utterance, and in part to the fact that where no resonance frequency is present in decided amplitude, the error due to the favored rates of the phonograph diaphragm is greatly increased.

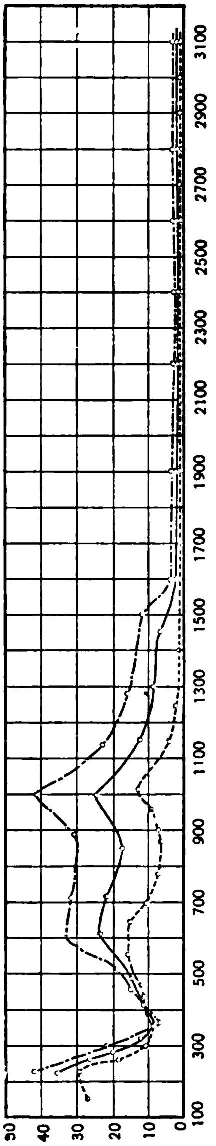

Fig. 2. *O* Resonance Curve.

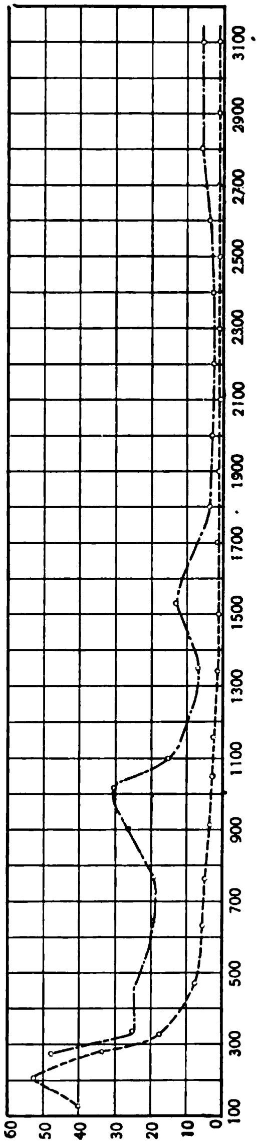

Fig. 3. *U* Resonance Curve.

Though I give the resonance curve therefore as before, I regard only the line for men as of great significance. One fact, however, is shown by the upper line, *i. e.*, the presence in many feminine *u*'s of a high resonance in the neighborhood of 3,000. This is present in some cases in considerable amplitude, so plainly in fact that many of the tones reveal it to the unaided eye at a casual examination. To this I have already alluded. I have not observed this in any of the men's *u*'s. Of course with low fundamental chord-tones, such a high resonance would not be prominent in the trace. Still, were it a characteristic mark of *u*-quality, its presence should be detected and its amplitudes should be capable of measurement. That it is an accidental resonance, whose absence does not impair the true *u*-quality is further shown by the fact, that many women's *u*'s are without it, and that its position is free to shift within considerable limits of pitch. In the resonance-curve computed on averages it raises slightly the end of the line all the way from 2,800 to about 3,300 as is seen in Fig. 3, page 83.

The normal *u* then will have strength in the chord-tone and in the first upper partial on lower fundamentals, and chiefly in the chord-tone on higher ones. The ear identifies it by the absence of marked upper resonances.

The analyses of the *o* curves are not so consistent, and their interpretation presents no little difficulty. If the individual analyses are studied one by one, the range will be found to be very wide. running from a typical and normal a^o to a fully closed *u*. For example, voice 6 at 144 is a good a^o-record, while voice 1 at 144 gives a record which is a normal man's *u*. Intermediate between these extremes all shades seem to be represented.

One reason of this is, I conclude, that there was little uniformity of utterance among the voices tested. The diphthongal character of *o* allows anything to pass with the ear, from $a^o\underset{\wedge}{u}$ to a true *o*. If the waves analyzed were taken from the earlier part of the utterance, the analyses should be more or less like a true a^o, if from the latter part, more or less like a true *u*. I conclude from this that the intermediate examples represent approximately the truth, and a true monophthonal *o* may be described phonetically as follows: It possesses a strong resonance at about 600 to the second, but none higher, also a resonance heard either as a chord-tone or as a first upper partial at about 225. These two resonances seem to be characteristic. A good example of such an *o* will be seen in voice 4 at 128, or in voice 5 at 288. In the first II. and V. are strongly reinforced, in the second I. and II. These facts are shown in the *o*-resonance curve (Fig. 2, page 83), but since this is computed from averaging all the records analyzed, it shows also a resonance at 1,000, due to the presence of many records which shade toward *a*°.

If these conclusions are correct, it becomes clear why reproducing a phonographic *u* at an increased speed, or an *a*° at a reduced speed, will not yield a satisfactory *o*-sound. In view of the inconsistencies of the records analyzed it is desirable that further researches be made with *o*-records, great care being taken in recording normal *o*-sounds, and also in selecting waves for measurement from different parts of the trace for careful comparison. This is of course absolutely essential in the study of diphthongs.

THE VOWEL *a*°.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.
		113	226	339	452	565	678	791	904	1017	1130	1243	1356	1469	1582	1695	1808	1921
1	119.8	32.0	16.8	1.1	3.7	16.6	15.8	3.6	1.2	2.9	1.3	0.4	0.7	0.8	1.4	1.2	0.3	0.2
4	69.9	2.0	30.7	2.1	2.0	5.9	18.7	3.9	7.3	13.4	1.1	1.6	1.5	2.7	0.7	0.7	1.2	0.2
		128	256	384	512	640	768	896	1024	1152	1280	1408	1536	1664	1792	1920	2048	2176
4	156.5	6.1	11.7	2.3	2.8	10.4	20.9	3.7	16.2	11.9	1.8	0.9	2.7	0.7	2.0	1.3	1.2	0.7
6	47.7	8.2	23.5	0.6	1.9	30.2	2.7	5.7	10.9	4.4	1.9	0.2	2.1	1.9	1.5	1.9	1.0	1.4
		144	288	432	576	720	864	1008	1152	1296	1440	1584	1728	1872	2016	2160	2304	2448
1	133.3	1.8	12.1	6.2	52.7	2.1	7.1	7.2	2.1	1.8	1.1	2.0	0.6	0.6	0.5	1.2	0.4	0.5
4	253.2	21.5	5.4	2.1	8.1	20.4	3.0	15.2	10.4	2.9	2.5	1.3	0.8	0.8	0.4	0.4	0.2	0.4
6	139.5	43.1	4.4	1.8	9.4	4.9	4.3	9.5	1.4	1.1	1.6	0.3	0.5	0.9	0.9	0.9	1.4	2.2
		160	320	480	640	800	960	1120	1280	1440	1600	1760	1920	2080	2240	2400	2560	2720
1	243.3	12.5	7.6	3.8	52.6	5.1	2.3	1.4	1.2	0.9	1.0	1.1	1.2	0.6	0.9	0.9	0.5	1.9
4	265.6	21.2	2.2	2.4	19.4	10.6	9.3	22.2	2.2	2.8	1.5	1.5	1.2	0.6	0.8	0.4	0.7	1.1
6	159.0	25.1	2.3	0.4	31.1	2.3	8.2	15.5	1.1	1.7	3.2	1.5	1.6	0.4	1.0	1.0	2.8	0.8
		171	342	513	684	855	1026	1197	1368	1539	1710	1881	2052	2223	2394	2565	2736	2907
1	173.6	24.9	8.8	9.2	21.5	11.1	7.5	1.7	0.9	0.6	0.6	1.1	0.3	0.3	0.6	1.0	2.8	1.4
4	343.9	20.5	2.4	4.8	18.6	4.0	30.2	5.2	4.8	2.9	1.4	0.5	0.8	0.4	0.5	0.3	1.1	1.6
6	84.6	6.4	6.3	13.9	7.2	8.9	16.9	2.7	4.1	1.4	1.5	2.7	2.4	2.5	6.5	10.2	5.6	0.8

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[1] Where the percentages do not sum up exactly to 100 it is because the computation included upper partials higher than those printed. In no cases are the omitted figures large enough to affect the statement of facts.

THE VOWEL *a°*, *continued*.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.
		192	384	576	768	960	1152	1344	1536	1728	1920	2112	2304	2496	2688	2880	3072	3264
1	261.0	19.9	6.9	33.6	18.7	10.0	1.5	0.4	0.8	0.8	1.2	0.4	0.4	0.8	0.8	1.5	0.8	1.5
4	295.9	18.6	3.4	5.7	18.9	10.3	28.8	2.6	3.7	0.5	2.0	0.5	0.8	0.2	0.4	1.1	1.7	0.8
6	154.4	23.4	9.1	4.5	10.9	6.2	14.2	1.7	3.8	1.7	6.9	0.6	0.9	2.7	5.1	3.8	2.0	2.5
7	39.0	34.6	8.7	0.5	9.2	2.6	28.7	1.0	3.8	2.1	0.6	2.0	1.0	1.3	0.6	0.3	1.5	1.5
		227	454	681	908	1135	1362	1589	1816	2043	2270	2497	2724	2951	3178	3405	3632	3859
1	524.0	20.4	9.4	24.7	26.7	4.0	4.6	0.8	0.8	0.8	0.8	1.4	1.5	1.2	1.5	0.4	0.4	0.6
4	307.5	23.7	8.7	33.3	12.1	9.2	3.4	1.2	2.1	0.4	0.2	0.7	1.7	0.4	1.1	0.9	0.7	0.2
6	157.2	20.2	8.6	21.6	17.1	4.6	4.6	0.1	1.8	0.5	4.5	4.5	3.2	2.9	3.2	0.5	0.5	0.6
7	63.1	30.3	7.1	15.1	9.4	4.4	4.6	2.4	2.4	2.2	1.4	4.6	8.3	3.5	2.7	0.8	0.2	0.6
		256	512	768	1024	1280	1536	1792	2048	2304	2560	2816	3072	3328	3584	3840	4096	4352
1	345.9	11.6	18.2	12.6	37.0	4.6	1.3	3.3	3.9	1.6	0.9	0.4	1.3	0.7	0.7	0.7	0.6	0.6
4	203.5	11.9	9.0	32.6	22.0	8.3	4.0	1.3	1.0	1.3	0.4	0.5	2.4	1.4	1.4	0.8	0.9	0.8
6	142.0	14.2	9.8	12.8	39.4	3.0	4.5	1.7	1.5	2.8	6.1	0.7	0.4	0.7	1.2	0.1	0.7	0.4
7	102.2	14.3	11.9	10.1	37.8	5.8	4.2	2.8	1.7	1.3	2.9	2.7	1.6	0.7	0.5	0.3	0.7	0.7
		288	576	864	1152	1440	1728	2016	2304	2592	2880	3168	3456	3744	4032	4320	4608	4896
7	95.8	9.7	39.8	10.2	9.0	7.9	3.4	2.6	1.6	3.7	4.0	2.2	2.9	0.5	0.8	0.4	0.8	0.5
11	82.9	15.2	9.2	24.2	12.3	16.5	3.3	3.3	1.6	2.0	1.3	1.3	2.0	1.6	2.2	1.0	1.6	1.4
		320	640	960	1280	1600	1920	2240	2560	2880	3200	3520	3840	4160	4480	4800	5120	5440
5	49.2	24.5	24.3	17.0	8.1	1.2	3.1	2.8	3.1	3.5	0.6	2.4	0.8	3.2	1.8	0.8	1.0	1.8
7	63.6	3.9	42.0	14.9	6.8	3.3	5.8	3.9	4.9	9.4	0.8	1.4	1.0	0.6	0.2	0.8	0.3	0.0
11	47.2	12.1	31.1	28.0	9.5	5.5	6.8	1.5	1.3	0.4	0.9	1.1	0.2	0.6	0.4	0.4	0.0	0.2
		342	684	1026	1368	1710	2052	2394	2736	3078	3420	3762	4104	4446	4788	5130	5472	5814
7	213.9	4.5	20.2	50.3	2.4	3.9	0.8	1.1	8.4	1.3	0.7	0.4	0.3	1.3	1.3	0.8	1.2	1.1
11	104.5	6.8	15.3	30.3	25.4	4.6	5.5	4.3	1.9	0.3	1.0	0.9	0.4	0.5	0.5	0.8	0.8	0.7
		384	768	1152	1536	1920	2304	2688	3072	3456	3840	4224	4608	4992	5376	5760	6144	6528
5	152.5	3.0	22.5	44.5	25.5	0.9	0.3	2.1	1.2									
7	93.5	7.2	25.1	32.8	3.2	6.1	1.5	3.2	7.3	1.0	0.7	2.4	1.3	1.3	1.7	1.8	1.8	1.6
11	311.3	6.8	18.1	51.4	17.9	0.7	2.0	2.1	1.0									
		454	908	1362	1816	2270	2724	3178	3632									
7	177.9	11.0	55.9	8.5	2.5	5.5	14.2	0.7	1.7									
11	252.0	8.0	56.3	21.9	2.1	1.6	1.9	5.4	2.8									
		512	1024	1536	2048	2560	3072	3584	4096									
5	121.7	4.9	60.2	18.5	5.2	1.8	6.5	0.8	2.0									
7	81.5	12.8	62.8	12.6	3.1	2.6	4.2	1.1	0.8									
11	276.1	10.2	49.8	29.2	4.7	2.3	1.3	1.5	1.0									

The Vowel *O*.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	XI.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.
		113	226	339	452	565	678	791	904	1017	1130	1243	1356	1469	1582	1695	1808	1921
1	55.0	42.2	11.5	10.2	2.8	12.7	0.9	1.6	0.8	0.8	1.3	1.1	1.3	1.8	1.8	1.1	0.8	1.1
6	89.2	15.3	39.8	9.2	15.3	2.6	7.6	1.0	1.2	0.8	0.8	1.0	1.0	0.2	0.8	0.6	0.3	0.3
		128	256	384	512	640	768	896	1024	1152	1280	1408	1536	1664	1792	1920	2048	2176
1	66.9	27.5	21.0	8.2	6.7	23.2	2.3	0.6	1.0	0.1	0.5	0.6	0.4	0.1	0.8	0.9	0.8	0.1
4	104.0	12.4	24.4	5.5	11.6	11.9	10.1	7.4	3.8	2.4	1.4	1.5	0.9	1.1	0.1	0.4	0.1	0.6
		144	288	432	576	720	864	1008	1152	1296	1440	1584	1728	1872	2016	2160	2304	2448
1	132.0	53.3	20.8	11.3	4.2	2.5	0.5	0.2	0.2	0.5	0.5	0.6	0.1	0.5	0.5	0.2	0.5	0.5
6	249.7	17.7	4.2	11.4	20.6	0.4	7.8	15.6	1.8	3.8	0.8	2.1	1.4	1.3	1.0	1.7	2.7	0.8
		160	320	480	640	800	960	1120	1280	1440	1600	1760	1920	2080	2240	2400	2560	2720
1	145.1	69.3	9.2	5.4	5.0	3.1	0.6	0.7	0.4	0.6	0.3	0.8	0.6	0.6	0.1	0.5	0.4	0.6
4	257.3	34.7	7.9	6.1	22.2	3.3	9.2	5.4	1.9	0.6	1.2	0.6	0.3	0.8	0.5	1.0	0.2	0.1
		171	342	513	684	855	1026	1197	1368	1539	1710	1881	2052	2223	2394	2565	2736	2907
1	152.0	18.5	25.7	11.1	25.6	1.6	2.5	1.0	1.0	0.7	0.3	0.6	0.7	0.6	1.4	0.9	1.6	1.8
4	164.5	28.6	5.8	17.4	9.2	9.0	12.4	4.5	1.4	1.4	0.7	0.8	0.7	0.8	0.4	0.7	0.9	1.7
6	357.1	12.9	7.9	17.2	6.7	8.5	28.2	0.8	1.9	0.2	1.9	1.6	3.0	3.2	1.3	1.5	1.5	1.7
		192	384	576	768	960	1152	1344	1536	1728	1920	2112	2304	2496	2688	2880	3072	3264
1	143.0	30.8	17.6	12.0	19.9	2.0	2.5	1.5	1.0	2.1	0.8	0.2	0.4	0.7	1.2	1.2	1.0	2.7
4	261.2	14.4	4.0	18.9	11.8	11.6	19.2	1.8	1.8	3.1	1.4	1.1	0.7	0.4	0.9	2.5	4.2	2.2
6	178.3	20.0	6.3	30.1	5.2	18.7	4.8	3.2	1.8	2.0	1.9	0.8	0.1	2.1	1.7	0.7	0.4	0.2
		227	454	681	908	1135	1362	1589	1816	2043	2270	2497	2724	2951	3178	3405	3632	3859
4	221.5	44.9	12.0	23.2	5.4	5.0	1.5	1.4	1.8	0.3	0.8	0.5	0.6	0.5	0.9	0.3	0.8	0.1
5	60.6	43.1	9.1	17.0	6.8	12.7	3.4	0.5	0.8	0.8	1.3	0.2	0.6	1.5	0.4	1.1	0.5	0.2
6	283.0	15.1	15.8	15.5	28.7	5.6	6.7	1.4	1.5	2.1	3.5	0.8	0.4	0.7	1.0	0.9	0.1	0.2
		256	512	768	1024	1280	1536	1792	2048	2304	2560	2816	3072	3328	3584	3840	4096	4352
1	221.7	13.3	22.0	3.1	49.0	4.2	1.7	1.2	1.2	0.5	1.3	0.4	0.1	1.3	0.2	0.3	0.1	0.1
4	288.1	27.6	31.1	16.9	9.8	3.4	2.9	0.7	0.1	0.6	0.7	1.6	1.1	1.4	1.1	0.5	0.3	0.2
6	339.6	10.5	14.8	8.2	45.5	3.0	5.1	1.1	1.9	0.9	2.9	0.8	1.4	0.7	1.9	0.6	0.4	0.3
		288	576	864	1152	1440	1728	2016	2304	2592	2880	3168	3456	3744	4032	4320	4608	4896
5	47.0	30.4	20.6	12.3	9.2	8.9	4.9	3.8	2.6	0.9	0.6	1.5	1.1	0.9	0.9	0.4	0.4	0.6
7	42.0	16.9	18.8	11.0	16.4	8.6	1.6	3.1	2.6	1.9	9.1	2.4	3.1	1.4	1.2	0.7	0.5	0.7
		320	640	960	1280	1600	1920	2240	2560	2880	3200	3520	3840	4160	4480	4800	5120	5440
5	42.6	39.8	15.6	5.5	21.9	2.3	2.3	2.1	2.3	0.9	0.9	1.6	0.9	0.9	0.9	1.4	0.5	0.2
7	107.7	7.4	46.8	11.4	8.0	5.4	4.8	4.1	3.3	4.8	1.6	0.5	0.3	0.4	0.3	0.6	0.1	0.2
11	85.6	13.6	40.1	17.8	16.9	4.8	2.2	1.1	0.4	0.5	0.9	0.4	0.3	0.2	0.2	0.1	0.1	0.4
		342	684	1026	1368	1710	2052	2394	2736									
5	238.6	4.3	26.4	47.4	18.7	0.7	1.0	0.9	0.6									
11	233.6	4.0	25.3	50.0	13.8	2.2	1.6	1.3	1.8									
		384	768	1152	1536	1920	2304	2688	3072	3456	3840	4224	4608	4992	5376	5760	6144	6528
5	134.4	10.1	51.6	18.5	11.7	2.4	1.6	0.8	0.9	0.2	0.4	0.2	0.1	0.4	0.3	0.4	0.3	0.
7	119.3	3.0	44.7	11.0	8.6	6.8	5.0	4.4	0.6	9.5	1.5	1.9	1.2	0.4	0.6	0.3	0.3	[illegible]
11	174.2	4.9	29.4	45.2	16.2	1.4	1.0	0.5	1.4									

The Vowel *O*, *continued.*

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.
		454	908	1362	1816	2270	2724	3178	3632									
5	121.2	17.1	62.7	12.3	2.8	1.8	2.0	0.7	0.6									
11	104.3	15.0	50.1	25.8	1.2	1.0	2.4	3.2	1.3									
7	382.6	18.2	52.5	9.6	2.1	2.5	11.1	2.7	1.3									
		512	1024	1536	2048	2560	3072	3584	4096	4608	5120	5632	6144	6656	7168	7680	8192	8704
5	116.4	11.6	33.6	32.1	10.3	4.4	1.4	0.4	2.1	6.7	0.9	0.5	0.2	0.7	0.1	0.1	3.3	0.5
7	155.6	23.7	62.7	6.5	3.1	1.2	1.5	0.6	0.7									
11	107.1	6.4	53.1	20.3	11.8	3.3	2.4	1.6	1.1									

The Vowel *U.*

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIX.	XX.	XXI.	XXII.
		113	226	339	452	565	678	791	904	1017	1130	1243	1356	1469	1582	1695	1808	1921
1	130.6	17.1	41.8	8.6	1.6	3.7	7.6	1.4	1.0	2.1	0.4	2.4	1.4	1.7	0.8	0.5	0.5	0.6
4	109.3	8.1	52.6	12.7	5.7	3.3	3.4	0.8	1.8	0.5	0.4	1.2	1.5	0.7	0.7	0.6	1.8	1.2
		128	256	384	512	640	768	896	1024	1152	1280	1408	1536	1664	1792	1920	2048	2176
1	124.8	37.6	28.6	5.2	2.4	6.5	4.0	0.4	1.9	0.4	0.6	0.6	0.6	1.4	0.8	0.2	0.6	0.9
4	26.7	3.0	39.1	10.0	9.0	3.7	2.7	3.4	2.6	0.8	1.5	3.4	1.9	4.9	1.9	2.2	1.5	1.2
		144	288	432	576	720	864	1008	1152	1296	1440	1584	1728	1872	2016	2160	2304	2448
1	274.3	63.6	16.7	2.0	2.9	1.9	3.6	1.6	0.4	1.1	0.4	0.4	0.0	0.4	0.3	0.8	0.3	0.7
4	225.3	54.7	19.0	8.7	1.6	2.6	3.5	1.8	0.9	0.1	0.7	1.9	0.9	1.0	0.4	0.2	0.2	1.0
6	312.9	59.1	18.1	7.2	0.9	1.4	3.6	2.2	0.4	0.5	1.1	0.9	0.3	0.5	1.0	1.3	0.5	0.6
		160	320	480	640	800	960	1120	1280	1440	1600	1760	1920	2080	2240	2400	2560	2720
1	216.1	45.3	23.0	2.8	14.6	2.5	1.7	1.4	0.4	0.1	0.8	0.6	0.6	0.5	1.0	2.3	1.0	1.4
6	292.3	64.8	18.0	4.4	2.6	0.2	2.0	2.6	0.5	1.1	0.3	0.5	0.1	0.2	0.5	0.9	0.2	0.5
		171	342	513	684	855	1026	1197	1368	1539	1710	1881	2052	2223	2394	2565	2736	2907
1	246.8	32.4	24.0	5.9	19.0	7.6	5.4	0.9	0.9	0.9	0.4	0.8	0.2	1.7	4.6	0.4	1.9	1.6
4	304.5	44.2	20.5	6.6	8.0	9.1	3.3	1.9	1.1	1.2	0.9	0.3	0.4	0.1	0.4	0.8	0.6	0.6
6	300.4	35.2	21.9	6.5	10.0	5.8	8.7	2.4	0.0	1.3	0.4	0.6	2.6	2.1	1.3	0.3	0.3	0.6
		192	384	576	768	960	1152	1344	1536	1728	1920	2112	2304	2496	2688	2880	3072	3264
1	347.0	34.0	28.8	4.5	14.8	2.9	1.7	1.6	0.5	2.3	0.5	1.1	1.1	3.4	0.4	1.2	0.8	0.4
4	185.9	65.3	14.4	4.4	4.9	2.9	0.8	1.5	0.4	0.5	0.4	0.6	1.0	0.3	0.4	0.5	0.4	0.4
6	330.5	30.5	21.5	5.6	6.6	1.9	18.8	1.0	1.8	0.5	1.4	2.0	3.0	1.0	0.6	1.5	0.7	1.6
		227	454	681	908	1135	1362	1589	1816	2043	2270	2497	2724	2951	3178	3405	3632	3859
1	554.0	74.7	3.6	14.3	1.3	1.4	0.5	1.1	0.3	0.4	0.6	0.2	0.3	0.1	0.2	0.7	0.1	0.2
4	442.6	70.4	7.1	8.2	5.9	1.5	1.3	0.3	0.8	0.9	0.5	1.0	0.2	0.2	0.3	0.2	0.3	0.9
6	197.5	54.8	22.2	7.0	2.9	2.2	1.0	1.0	2.1	4.1	0.8	0.3	0.1	0.2	0.4	0.5	0.3	0.1

The Vowel *U*, *continued.*

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XVI.	XV.	XVI.	XVII.
		256	512	768	1024	1280	1536	1792	2048	2304	2560	2816	3072	3328	3584	3840	4096	4352
1	455.0	41.8	13.5	19.3	2.5	2.1	2.7	0.8	1.1	5.0	1.3	4.3	2.0	1.3	0.5	0.5	0.2	1.3
4	191.1	66.9	8.6	12.9	3.9	1.7	0.9	1.1	0.4	0.4	0.7	0.3	0.3	0.3	0.9	0.4	0.2	0.3
6	181.9	56.5	14.7	17.2	3.6	1.5	1.4	0.7	1.1	0.6	0.6	0.7	0.3	0.2	0.4	0.1	0.1	0.3
5	72.1	74.7	0.8	4.2	3.0	0.7	0.5	1.7	0.1	1.7	1.4	3.2	2.2	1.9	1.5	1.2	0.5	0.7
		288	576	864	1152	1440	1728	2016	2304	2592	2880	3168	3456	3744	4032	4320	4608	4896
7	47.7	22.9	13.0	5.7	5.6	5.4	4.2	3.8	2.5	6.0	6.1	14.9	4.8	0.6	1.7	0.2	1.1	1.5
		320	640	960	1280	1600	1920	2240	2560	2880	3200	3520	3840	4160	4480	4800	5120	5440
11	49.2	34.9	39.2	8.9	4.0	5.6	1.8	0.4	0.8	0.6	0.8	0.4	0.2	1.0	0.8	0.2	0.2	0.2
		342	684	1026	1368	1710	2052	2394	2736	3078	3420	3762	4104	4446	4788	5130	5472	5814
5	121.9	29.5	5.3	49.2	2.4	4.4	3.5	1.1	4.6									
7	58.7	13.8	14.8	24.3	6.5	6.3	1.5	1.9	15.3	8.5	1.4	1.0	0.7	1.0	0.7	1.2	0.7	0.4
11	54.5	16.0	24.2	51.5	3.1	2.2	0.4	1.3	1.3									
		384	768	1152	1536	1920	2304	2688	3072	3456	3840	4224	4608	4992	5376	5760	6144	6528
5	103.7	30.1	2.0	11.3	38.5	4.8	2.2	2.4	2.3	1.0	0.8	0.5	0.7	1.0	0.7	0.8	0.3	0.6
7	70.6	21.1	35.6	11.3	5.2	4.8	2.4	2.0	1.7	4.5	3.5	3.4	1.1	1.4	0.1	0.3	0.8	0.8
11	46.8	27.2	36.3	28.4	2.1	1.5	2.1	0.9	1.5									
		454	908	1362	1816	2270	2724	3178	3632	4086	4540	4994	5448	5902	6356	6810	7264	7718
5	243.9	39.4	45.0	9.1	0.4	2.3	2.7	0.2	0.9									
7	65.4	19.4	29.7	12.3	4.3	4.4	15.6	6.6	1.1	1.9	0.6	0.9	0.6	0.6	0.5	0.5	0.5	0.5
11	82.8	29.7	45.8	15.5	5.7	1.4	0.6	0.9	0.4									
		512	1024	1536	2048	2560	3072	3584	4096	4608	5120	5632	6144	6656	7168	7680	8192	8704
7	124.8	28.2	32.1	19.6	3.4	3.9	7.1	1.5	0.6	0.4	0.6	0.5	0.4	0.4	0.3	0.4	0.4	0.2
7	47.0	21.7	19.2	18.1	4.7	5.9	12.1	7.9	3.2	1.1	1.2	0.2	1.1	0.2	0.9	1.0	0.6	0.9

THE MEASUREMENT OF INDUCTANCE AND CAPACITY BY MEANS OF THE DIFFERENTIAL BALLISTIC GALVANOMETER.

By William J. Raymond.

THE differential galvanometer has long been used in the comparison of electric resistances, but apparently has not been employed to any great extent in the measurement of inductance and capacity. Believing that it deserves a more prominent place in electrical laboratories than has yet been given to it, the following descriptions of a number of methods for the determination of self-inductance, mutual inductance and capacity have been prepared. Some of these are null methods, others require the measurement of ballistic deflections of the needle of the galvanometer. Including three methods previously published by Kohlrausch and Niven, all have been tested by the present writer. He has not discovered in the literature of the subject any other methods which make use of the differential galvanometer.

The differential telephone[1] and differential transformer[2] have recently been employed in the measurement of inductance and capacity with great precision in the expression of results. The methods described are necessarily null methods, and make use of a system of conductors analogous to the Wheatstone quadrilateral, or a somewhat simpler, parallel arrangement of branches containing the coils of the telephone or transformer. The double condition of equality of amplitude and phase of alternating currents in the differential coils is required for silence in the telephone. Possibly in some of the null methods described in the present paper, the telephone may replace the galvanometer with gain in precision of measurements. Apparently in most of the methods the double condition can not be reached.

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[1] Ho, Electrical World, 41, p. 884, 1903; Ho, PHYS. REV., XIX., p. 166, 1904; Duane and Lory, PHYS. REV., XVIII., p. 275, 1904.

[2] Trowbridge, PHYS. REV., XX., p. 65, 1905.

In laboratories and testing rooms reasonably free from magnetic disturbances, a galvanometer of the form subsequently described may be employed. In localities where there are fluctuations in magnetic field, a galvanometer of the D'Arsonval type, differentially wound, may be found practicable. A differential galvanometer of this type was described at the meeting of the American Physical Society, held at St. Louis in September, 1904.[1] It appears that most if not all of the methods of measurement given in the present paper may be carried out with such a galvanometer, designed for ballistic use. The damping factor for the vibration of the coil should be made as small as possible, and its period should be rather long.

Working formulas given in this paper are easily deduced from equations of electromotive force, as exemplified in method 1. In nearly all cases current divides between parallel branches connecting points A and B. Expressions for difference of potential by way of the branches between A and B, during the period of variable currents, are equated, and integrated over this period. This leads to an equation connecting inductances or capacities, resistances, quantities of electricity passing through the coils of the galvanometer, and final, steady currents. Equality of final currents permits the cancelation of equal terms, and in the null methods the condition of equality of quantities passing through the galvanometer is introduced. In deflection methods difference between quantities is written as proportional to the deflection of the needle of the galvanometer. The proportional factor need not be known since it disappears by cancelation from ratios of deflections. When there are more than two branch circuits, ratios of steady currents are expressed as ratios of resistances. The charge of a condenser is written as capacity multiplied by difference of potenial the latter factor appearing as current multiplied by resistance, when resistance is one of the parallel branches connects the terminals of the condenser.

Accuracy of results obtainable by the methods described in this paper rests upon a number of factors, some of which are apparent from inspection of working formulas. The writer was more concerned to survey the whole field than to investigate the accuracy which may be obtained by any one method. Yet in this general survey, among separate measured values of the same quantity, agreement within two or three tenths of one per cent. was reached, not only in one method but among several. It appears that with care agreement within one tenth per cent. may be easily reached, especially among the null methods. With closer attention to detail, still better results may be expected. The question of accuracy of standards is not touched upon here, but merely the precision of measurements, that is, the agreement among individual results.

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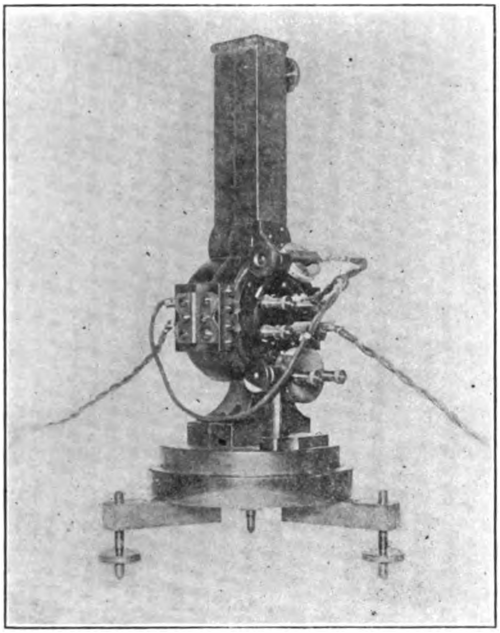
[1] J. C. Shedd, Phys. Rev., XIX., p. 301 (abstract).

DESCRIPTION OF GALVANOMETER.

The galvanometer used in this work was constructed by Mr. Stamper, the mechanician in the department of physics of the University of California. Two coils are contained, one in the upright standard of the instrument, one in a hinged portion, so arranged as to permit free access to the needle and suspending fiber. Each coil was wound by laying two wires side by side, and keeping them together from beginning to end. This insured nearly equal values of magnetic effect, of self-inductance and of resistance of the windings. When the four windings, constituted as described, and numbered 1 and 2 in the hinged part of the galvanometer, and 3 and 4 in the fixed standard, were connected in series, 1 and 3 opposing 2 and 4, the deflection of the needle was 12 minutes of arc when the current flowing was 0.15 ampere. It was considered desirable to secure more exact magnetic balance. To this end a small accessory coil of three turns of wire was mounted at the back of the galvanometer and connected in series with windings 1 and 3. This coil turns on a horizontal axis and is easily adjusted so that there is no deflection of the needle when the four windings are connected as previously described and traversed by steady current many times greater than is used in the measurement of inductance or capacity. The coils are connected externally by double conductors so that possible displacement of wires during the progress of a measurement may have no effect upon the magnetic balance. The self-inductances of the coils of the galvanometer are assumed equal in the deduction of working formulas. In the instrument described they were found to be close enough in value for the immediate purpose of the investigation, without further adjustment. If necessary a pair of small coils, mounted according to the plan of the Ayrton and Perry variable standard of inductance, may be placed at a safe distance from the needle of the galvanometer and connected in series with the coil having the smaller self-inductance. The resistance of the four windings of the galvanometer, connected in series, is 12.9 ohms at 16° C. Adjustment of the branch circuits to equality of resistances is reached by the plan described under the first of the following methods of measurement.



The suspended system or needle of the galvanometer consists of an ellipsoidal magnet, 6.5 mm. in diameter, mounted on a sliver of bamboo. A small mirror is carried at the upper end of the bamboo stem and just below the mirror is a thin brass disk, 16 mm. in diameter, turned with a heavy rim to secure large moment of inertia with small mass. The whole is hung from a silk fiber. The purpose of the brass disk is to increase the period of vibration of the needle, for convenience in reading turning points on the telescope-scale in the deflection methods. Ballistic deflection of the needle for given magnetic impulse of current passing is thereby reduced in the same proportion as the period is increased, so that in practice one has to strike a balance between convenience of use and sensitiveness. To bring the needle to rest rapidly and effectively, just before a ballistic deflection is to be measured, a second accessory coil of 3.7 cm. diameter and 15 turns of wire is mounted back of the instrument and made part of an independent circuit through a battery cell and a double key, placed within reach of the observer's hand. One key closes the circuit through 150 ohms resistance mounted on the base of the key; the second key shunts out this resistance when a stronger, temporary, controlling field is desired at the needle. To vary the controlling field further the plane of the accessory coil may be turned about a horizontal axis. Thus when the needle is vibrating through large angles the stronger field, applied at the proper time, rapidly reduces the swing. When the needle is nearly at rest a weaker field is desirable.

When the most favorable conditions for securing accuracy of results are considered, it must be at once evident that the galvanometer here described is adapted to a limited range of measurements, because its resistance is small. Notably in the measurement of capacities and of inductances associated with large resistances, a more sensitive galvanometer would be required. In neither of the cases cited would increased resistance of the galvanometer, due to the use of a greater number of turns of finer wire, be objectionable, while the deflection of the needle when there is a given difference between the quantities of electricity passing through the two coils, would be greatly increased. If necessary, further increase of sensitiveness may be reached by known methods, such for example as the use of an astatic needle.

METHODS OF MEASUREMENT.

All of the methods to be described are essentially comparisons between any two of the four quantities, resistance, self-inductance, mutual inductance and capacity. Incidentally measurements of period of vibration of the galvanometer needle and of ballistic deflection are involved. About half of the methods are null methods which seek for adjustment securing balance between impulses of opposing force-moments exerted upon the needle, the impulses integrated over the period of variable current, and both impulses of extremely short duration. Since four quantities may be combined, two and two, in ten different ways, a convenient classification of methods is suggested. These classes are the comparison of two resistances; two self-inductances; two mutual inductances; two capacities; resistance and self-inductance; resistance and mutual inductance; resistance and capacity; self-inductance and mutual inductance; self-inductance and capacity; mutual inductance and capacity. Comparison of resistances with the differential galvanometer, using steady currents, is so familiar that no further reference will here be made to it. The methods described in this paper will then fall into the remaining nine classes. They are doubtless not all which might be devised, but will serve as illustrative examples, covering fairly well the usual range of measurements.

When dealing with inductive resistances, the usual precautions are to be observed. Coils must be sufficiently separated to avoid mutual magnetic effect, and their positions and distances should be such that no effect is perceivable at the galvanometer. A reversing key or commutator is placed in the battery circuit, instead of a simple key merely to open or close the circuit. In this connection Lord Rayleigh[1] remarks that: "A reversal has two advantages over a simple make or break. In the first place the effect is doubled and is therefore more easily measured; and in the second the battery is more likely to work in a uniform manner, the circuit being always closed except for a fraction of a second at the instant of reversal." It may be added that if the damping of the needle differs sensibly between open and closed circuit through the galvanometer, the correction for it will be considerably simplified.

DESCRIPTION OF METHODS.

Method 1, Comparison of Self-Inductances.—(Fig. 1.) A battery cell and commutator K are arranged to send current from A to B through a divided circuit. On one side are the inductive resistance

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[1] Phil. Trans. R. S., 1882, Part II., p. 678.

L_1 (or L_2), a box of non-inductive resistance coils, and windings 1 and 3 of the galvanometer, represented in the figure by a circle; on the other side a resistance box, and windings 2 and 4 of the galvanometer, represented by the second circle. B is a contact key which may be moved at will along a german silver wire CD, 50 centimeters in length, to secure adjustment to exact equality of the total resistances, R_1 and R_2, on the two sides. Resistance may be included in the battery branch if necessary for ballast. (*a*) With inductance L_1 in circuit, balance the resistances for zero deflection of the galvanometer needle, using steady current. Then R_1 is equal to R_2. (*b*) Bring the needle of the galvanometer to rest, reverse the commutator K and measure the ballistic deflection d_1. (*c*) Insert the inductance L_2 in place of L_1 and adjust the resistance in series with it to balance the same resistance R_2 previously used. (*d*) Reverse the commutator as before and measure the ballistic deflection d_2. The ratio of inductances is then

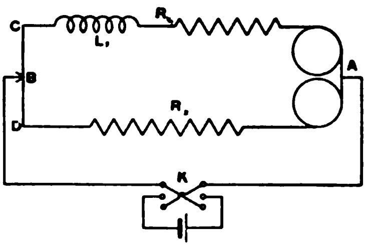

Fig. 1.

$$\frac{L_1}{L_2} = \frac{d_1}{d_2}. \tag{1}$$

To deduce this expression, write the difference of potential between A and B for any time during the period of variable currents,

$$R_1 i_1 + L_1 \frac{di_1}{dt} + \Gamma \frac{di_1}{dt} - M \frac{di_2}{dt} = R_2 i_2 + \Gamma \frac{di_2}{dt} - M \frac{di_1}{dt}, \tag{2}$$

in which Γ is the self-inductance of galvanometer windings 1 and 3, or 2 and 4, M is their mutual inductance, and i with indicating subscript is current intensity. Integrating over the period of variable currents,

$$R_1 Q_1 + L_1 I_1 + \Gamma I_1 - M I_2 = R_2 Q_2 + \Gamma I_2 - M I_1, \tag{3}$$

in which I_1 and I_2 are final, equal, steady currents, and Q_1 and Q_2 are quantities of electricity passing through the coils of the galvanometer during the period of variable flow. Canceling equal terms and dropping unnecessary subscripts,

$$Q_2 - Q_1 = \frac{L_1 I}{R}. \tag{4}$$

Similarly, from operations (*c*) and (*d*),

$$Q_2' - Q_1' = \frac{L_2 I}{R}. \tag{5}$$

The differential quantities are proportional to the ballistic deflections d_1 and d_2, the proportional factor involving the period of vibration of the needle of the galvanometer and constants of the coils. The deflections need not be corrected for damping, and are measured either in radians or directly in centimeters on a scale, provided that the telescope remains at a fixed distance from the galvanometer.

$$\frac{Q_2 - Q_1}{Q_2' - Q_1'} = \frac{d_1}{d_2} = \frac{L_1}{L_2}. \tag{6}$$

Method 2, Comparison of Self-Inductances.—This is a null method due to Professor C. Niven.[1] Coils whose inductances are L_1 and L_2 (L_1 greater than L_2), are joined in series with non-inductive resistances and connected one on each side of the galvanometer circuit. Referring to the similar arrangement of Fig. 2, L_1 is placed nearer the point C than its series resistance, L_2 nearer the galvanometer, and R_2 is omitted. If each non-inductive resistance is made equal to the resistance of the opposing coil, there will be no permanent deflection of the needle of the galvanometer when steady current is applied. Further, points between the coils and the series resistances are at the same potential, and may be joined by a cross-wire without disturbing balance for steady currents. If the resistance of this cross-connection is adjustable, a value S will be found by trial, such that there is no ballistic deflection of the needle of the galvanometer, when current is reversed by means of the commutator K. If R_1 is the resistance between point B and the connection joining L_1 and its series resistance, the ratio of inductances is

$$\frac{L_1}{L_2} = \frac{2R_1 + S}{S}. \tag{7}$$

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[1] Niven, Phil. Mag. (5), Vol. 24, p. 234, 1887; Gray, Abs. Meas. in El. and Mag., Vol. 2, p. 463, 1893.

Method 3, Comparison of Self-Inductances.—This is a null method for which the scheme of connections is indicated in Fig. 2. If the resistance of one of the coils, R_1, is considerably greater than that of the other, the non-inductive resistance in series with R_1 may be omitted. The resistances are first to be balanced for steady currents; then adjusted for zero ballistic deflection when commutator K is reversed. Since balance for steady currents is to be maintained, this will require double adjustment of resistance R_2, in parallel with R_1, and one of the series resistances. With inductances of ordinary magnitude, it will be found that near the final adjustment of R_2 small changes in series resistances will suffice to maintain balance for steady currents. These changes may be made by shifting contact B along the german silver wire CD. If there is difficulty in deciding upon the best value of R_2 for zero ballistic deflection, the usual method of interpolation between values giving small right and left deflections may be employed. The ratio of inductances is

$$\frac{L_1}{L_2} = \frac{(R_1 + R_2)^2}{R_2^2}. \tag{8}$$

This equation may be easily deduced from an equation of electromotive forces by the plan followed in the establishment of equation (1).

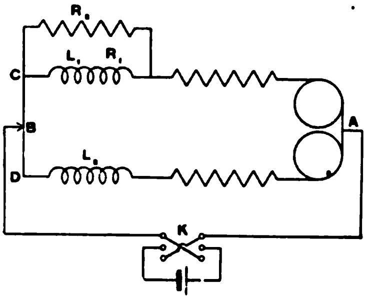

Fig. 2.

Method 4, Comparison of Mutual Inductances, Null Method.—(Fig. 3.) Four coils, whose self-inductances are denoted by L_1, L_2, L_3 and L_4, and mutual inductances by M_{12} and M_{34}, are connected, together with non-inductive resistances and the differential galvanometer, as indicated in the figure. (*a*) Balance the resistances for zero deflection of the needle of the galvanometer, using steady currents. (*b*) Connect the coils so that the magnetic fields of coils 3 and 4 shall coincide in direction, while the fields of coils 1 and 2 are opposed when current flows from A to B. Adjust the resistances in series with coils 1 and 4 so that there may be no ballistic deflection when the commutator K is reversed. (c) Connect the coils so that the magnetic fields of both pairs shall be opposed in direction, and again adjust for zero ballistic deflection. Interpolation may be employed to obtain the best values of resistances. If R_1 denotes the total resistance from A to B by way of coil 1, and R_4 denotes the total resistance by way of coil 4 in adjustment (b); and R_1' and R_4' denote corresponding values in adjustment (c); then the ratio of mutual inductances is

$$\frac{M_{12}}{M_{34}} = \frac{R_1 R_1' (R_4 + R_4')}{R_4 R_4' (R_1 - R_1')}. \qquad (9)$$

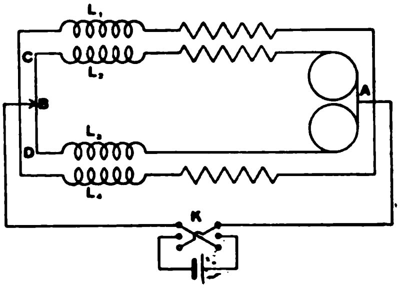

Fig. 3.

With other magnitudes of mutual inductances and self-inductances than those employed by the writer, other connections than those described under (b) and (c) may be required. Corresponding changes in the signs of the working formula will then be necessary.

Method 5, Comparison of Mutual Inductances, Deflection Method.—Connect coils 1 and 2, whose mutual inductance is M_{12}, in series on one side of the divided circuit of the galvanometer; and coils 3 and 4, whose mutual inductance is M_{34}, on the other side. (a) Insert non-inductive resistance in the branch of the circuit having the lesser total resistance, and balance for steady currents. (b) With the magnetic fields of both pairs of coils coinciding in direction when current is flowing, reverse the commutator K and measure the ballistic deflection d_1. (c) Reverse the terminals of coil 3, so that its field may oppose that of coil 4, and measure the ballistic deflection d_2, obtained by reversal of the commutator. (d) Interchange the terminals of coil 1 so that its field may oppose that of coil 2, and measure the ballistic deflection d_3, obtained by reversal of the commutator. The required ratio of mutual inductances is

$$\frac{M_{12}}{M_{34}} = \frac{d_2 - d_3}{d_2 - d_1}. \qquad (10)$$

The signs in this equation depend upon the order in which the terminals are interchanged in operations (b), (c) and (d).

Method 6, Comparison of Capacities, Null Method. — Equal, non-inductive resistances are connected as indicated in Fig. 4. The sliding contact B is adjusted for final balance of resistances, shown by zero deflection with steady current. Condensers 1 and 2, whose capacities are C_1 and C_2, are joined as indicated, one side of each connected to a traveling plug, so that each condenser may be put in parallel with any required portion of the corresponding resistance. If R_1 and R_2 are the resistances thus bridged between point B and the traveling plugs, when the ballistic deflection of the galvanometer is zero, the ratio of capacities is

$$\frac{C_1}{C_2} = \frac{R_2^2}{R_1^2}. \qquad (11)$$

Method 7, Comparison of Capacities. — This is a null method for which the scheme of connections is indicated in Fig. 5. Condensers 1 and 2 are placed as shown with non-inductive resistances in series, to avoid too heavy discharge currents through the coils of the galvanometer. A battery of several cells is connected to a resistance of twenty thousand ohms or more, through a commutator K. Traveling plugs A_1 and A_2 permit the bridging of resistances R_1 and R_2 as shown. By trial the plugs are placed so that the ballistic deflection of the needle of the galvanometer is zero when the commutator is reversed. The ratio of capacities is

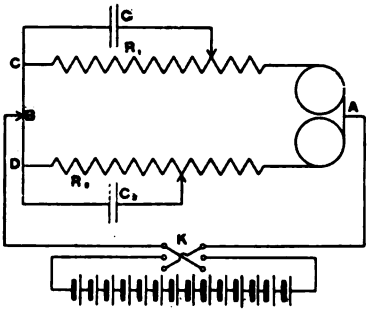

Fig. 4.

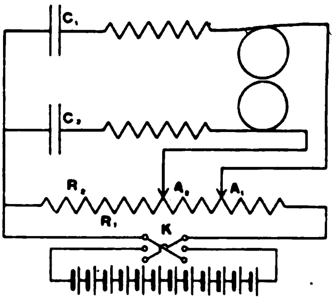

Fig. 5.

$$\frac{C_1}{C_2} = \frac{R_2}{R_1}. \qquad (12)$$

Method 8, Comparison of Capacities. — This null method is a modification of the last. Double contact keys are arranged to charge the condensers 1 and 2 when the keys are depressed; and to discharge each condenser through one coil of the galvanometer when they are simultaneously released. The lower contact points of the keys are connected, one to each of two traveling plugs A_1 and A_2, placed as in method 7, and the upper contact points are connected to resistances in the branches of the galvanometer circuit. The discharge currents pass through the coils of the galvanometer when the keys are released, unite and pass through a common wire to the plates of the condensers which are not in connection with the keys. These plates are also joined to one end of the high resistance as in method 7. This arrangement avoids in a measure the trouble arising from faulty insulation of either condenser.

Method 9, Comparison of Capacities, Deflection Method. — Referring to Fig. 2, replace each inductive resistance by one of the two condensers whose capacities C_1 and C_2 are to be compared, and omit the shunt resistance R_2. A battery of several cells will in general be required, instead of the single cell shown in the figure. (*a*) Reverse the commutator K and measure the ballistic deflection d_1. (*b*) Remove both condensers from the branches of the circuit, leaving only non-inductive resistances in series with the coils of the galvanometer. Join the condensers in parallel with each other and with one of the resistances R_1. Adjust the other resistance and the sliding contact B to obtain zero deflection when steady current is flowing. The total resistance from A to B by either branch is now R. (*c*) Reverse the commutator K and measure the ballistic deflection d_2. The ratio of capacities is

$$\frac{C_1}{C_2} = \frac{2R^2 d_2 + R_1^2 d_1}{2R^2 d_2 - R_1^2 d_1}. \tag{13}$$

The same battery is used throughout and its internal resistance is negligible in comparison with R. The signs in the formula assume that the capacity of condenser 1 is greater than that of condenser 2.

Method 10, Self-Inductance Measured in Henrys. — This is a deflection method of comparing self-inductance and resistance, analogous to Maxwell's method as modified and employed by Lord

Rayleigh and Dr. Schuster in their work on the determination of the ohm in absolute measure.[1] The connections of Fig. 1 are used. (*a*) Balance the resistances for zero deflection when steady current is flowing. (*b*) Reverse the commutator K and measure the resulting ballistic deflection d_1. This deflection is to be corrected in the usual way to the value which would have been found, if there had been no damping. (*c*) Change the resistance on one side of the circuit between A and B by a small amount ΔR, and measure the resulting deflection d_2 when steady current is flowing. If R is the total resistance on each side before the change, and T is the measured period of vibration of the needle of the galvanometer, the inductance is

$$L = \frac{\Delta R \cdot R}{R + \Delta R} \cdot \frac{T}{4\pi} \cdot \frac{d_1}{d_2}. \tag{14}$$

It is of interest to note that the dimensions of inductance (a length) appear in this equation as resistance (velocity) multiplied by time.

Method 11, Self-Inductance Measured in Henrys, Kohlrausch's Deflection Method, Using Induced Currents.[2] — The coil whose self-inductance is to be determined is connected in one branch of the differential galvanometer circuit as shown in Fig. 1, and an equal, non-inductive resistance is included in the other branch. Points A and B are connected to a Weber magnet-inductor, or to the secondary of an induction coil. (*a*) By this means an induced current of short duration is divided between the branches of the galvanometer circuit. The quantity of electricity passing through each branch is the same, but since current grows more slowly on the side having the larger inductance, there is a sharp movement of the galvanometer needle from rest in its position of equilibrium, to another, momentary position of rest. This measured deflection is d_1. (*b*) By sending induced current from the same source as before through half of the windings of the differential galvanometer, connected in series with a large resistance, a ballistic deflection is obtained and measured. This is to be corrected for damping. Its corrected value is d_2. Let R_1 be the resistance of the coil whose inductance is desired, or of the equal, non-inductive ballast; R_2 the resistance of each half of the galvanometer; R_3 the resistance of the source of induced current; R_4 the large resistance included in part (*b*); T the period of vibration of the needle of the galvanometer. The required inductance is

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[1] Proc. R. S. London, Vol. 32, p. 116, 1881; Phil. Trans. R. S. London, 1882, Part II., p. 677.

[2] Ann. d. Phys. u. Chem., Vol. 31, p. 594, 1887.

$$L = \frac{d_1}{d_2} \cdot \frac{T}{2\pi} \cdot \frac{(R_1 + R_2)(2R_3 + R_1 + R_2)}{R_4 + R_3 + R_2}. \tag{15}$$

Method 12, Mutual Inductance Measured in Henrys, Deflection Method. — Two coils are connected in series, first with their magnetic fields coinciding in direction when current flows in a given direction, second with their fields opposed. If L_1, L_2 and M are the self-inductances and mutual inductance of the two coils, the total inductance is $L_1 + L_2 + 2M$ in the first case and $L_1 + L_2 - 2M$ in the second case. Measure these total inductances by method 10, each in henrys. The required mutual inductance is one fourth of the difference between the measured values.

Method 13, Capacity Measured in Farads.— This is a deflection method of comparing capacity and resistance. The condenser, whose capacity C is to be determined, is connected in parallel with non-inductive resistance and introduced into one branch of the galvanometer circuit, in place of capacity C_1 as shown in Fig. 4, C_2 being omitted. (*a*) Balance the resistances for zero deflection, using steady current. (*b*) Reverse the commutator K and measure the ballistic deflection resulting. Let this when corrected for damping be d_1. (*c*) Change one of the resistances by a small amount ΔR and measure the permanent deflection d_2, using steady current. Let R be the total resistance from A to B by either branch before the change; R_1 the resistance in parallel with the condenser; and T the period of vibration of the needle of the galvanometer. The required capacity is

$$C = \frac{\Delta R \cdot R}{R_1^2(R + \Delta R)} \cdot \frac{T}{4\pi} \cdot \frac{d_1}{d_2}. \tag{16}$$

Method 14, Comparison of the Mutual Inductance of Two Coils with the Self-Inductance of One of Them, Null Method. — Coils 1 and 2, whose self-inductances are L_1 and L_2 and whose mutual inductance is M, are connected as indicated in Fig. 6. For given direction of current from A to B, the magnetic fields of the coils are to be opposed in direction. (*a*) Balance the resistances for zero deflection, using steady currents. (*b*) Having connected non-inductive resistance in series with coil 2, adjust this resistance for zero ballistic deflection when the commutator K is reversed. If R_1 and R_2 are the total resistances from A to B by way of the branches including coils 1 and 2 respectively, the ratio of the self-inductance of coil 1 to the mutual inductance of both coils is

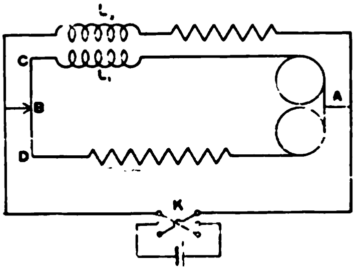

Fig. 6.

$$\frac{L_1}{M} = \frac{R_1}{R_2}. \tag{17}$$

Method 15, Comparison of the Mutual Inductance of Two Coils with the Self-Inductance of One of Them, Deflection Method. — The coils, whose self-inductances are L_1 and L_2 and whose mutual inductance is M, are connected in series and included in one branch of the galvanometer circuit, in place of L_1 in Fig. 1. (*a*) Balance the resistances for zero deflection when steady current is used. (*b*) Connect the coils so that their total inductance is $L_1 + L_2 + 2M$. Reverse the commutator K and measure the ballistic deflection d_1. (*c*) Connect the coils so that their total inductance is $L_1 + L_2 - 2M$. Reverse the commutator K and measure the ballistic deflection d_2. (*d*) Rearrange the connections according to the scheme indicated in Fig. 2, one coil in each branch of the galvanometer circuit. R_2 is omitted and the total resistance R, from A to B, is made the same as in parts (*a*), (*b*) and (*c*). After balancing the resistances for zero deflection with steady current, reverse the commutator K and measure the ballistic deflection d_3. The required ratios are

$$\frac{M}{L_1} = \frac{d_1 - d_2}{d_1 + d_2 + 2d_3}, \qquad \frac{M}{L_2} = \frac{d_1 - d_2}{d_1 + d_2 - 2d_3}. \tag{18}$$

L_1 is assumed greater than L_2 in the derivation of these equations.

Method 16, Comparison of the Mutual Inductance of Two Coils with the Self-Inductance of a Third Coil, Null Method. — Coils 1 and 2, whose self-inductances are L_1 and L_2 and whose mutual inductance is M_{12}, are connected according to the scheme indicated in Fig. 6, coil 1 in one branch of the galvanometer circuit. Coil 3, whose self-inductance is L_3, is included in the other branch of the galvanometer circuit. Non-inductive resistance is connected in series with coil 2 and with either coil 1 or 3 as may be necessary. (*a*) Balance the resistances in the branches of the galvanometer circuit for zero deflection, using steady current. (*b*) Adjust the resistance in series with coil 2 to obtain zero ballistic deflection when the commutator K is reversed. If L_1 is greater than L_3 the magnetic fields of coils 1 and 2 must be opposed; if L_1 is less than L_3 the fields must coincide in direction. (*c*) Transfer coil 3 to a position in series with coil 1, leaving coil 2 in its former place, and again balance the resistances for steady currents. (*d*) Repeat adjustment (*b*) with the new arrangement of coils. The magnetic fields of coils 1 and 2 are now opposed in direction. If R_1 and R_2 are the total resistances from A to B by way of the branch circuits containing coils 1 and 2 respectively, for adjustment (*b*); and R_1' and R_2' are the corresponding resistances for adjustment (*d*); the required ratio of inductances is

$$\frac{L_3}{M_{12}} = \frac{R_1'R_2 \mp R_1R_2'}{2R_2R_2'}. \tag{19}$$

The choice of sign depends upon the relative magnitudes of L_1 and L_3.

Method 17, Comparison of the Mutual Inductance of Two Coils with the Self-Inductance of a Third Coil.—The mutual inductance of two coils, M_{12}, is to be compared with the self-inductance of a third coil L_3. Connect coils 1 and 2 in series in one branch of the galvanometer circuit; and coil 3 in the other branch. By preliminary trial test the relative magnitudes of L_3 and the total inductance $L_1 + L_2 + 2M_{12}$. Connect non-inductive resistance in parallel with the larger of these inductances, and determine according to method 3 the ratio $(L_1 + L_2 + 2M_{12})/L_3$. This assumes that coils 1 and 2 are connected so that their magnetic fields coincide in direction. Keeping coils 1 and 2 in series, interchange the terminals of one of them so that their fields are opposed, and determine by the same method as before the ratio $(L_1 + L_2 - 2M_{12})/L_3$. The difference between the ratios thus determined is four times the required ratio of M_{12} to L_3.

Method 18, Comparison of the Mutual Inductance of Two Coils with the Self-Inductance of a Third Coil, Deflection Method.—Connect the three coils as in the last method, omitting the resistance in parallel with the larger total inductance. (*a*) Balance the resistances for zero deflection, using steady current. (*b*) Connect coils 1 and 2 so that their magnetic fields coincide in direction and measure the ballistic deflection d_1, obtained when the commutator K is reversed. (*c*) Connect coils 1 and 2 so that their magnetic fields are opposed in direction and measure the ballistic deflection d_2, obtained when the commutator is reversed. (*d*) Transfer coil 3 to a position in series with coils 1 and 2, altering resistances in series so that the total resistances from A to B by either branch of the circuit may be the same as they were in measurements (*b*) and (*c*). With the magnetic fields of coils 1 and 2 coinciding in direction, measure the ballistic deflection d_3, obtained when the commutator is reversed. (*e*) With the coils arranged as in (*d*), except that the fields of coils 1 and 2 are now opposed in direction, measure the ballistic deflection d_4. The required ratio is

$$\frac{M_{12}}{L_3} = \frac{(d_2 - d_1 - d_3 + d_4)}{2(d_1 + d_2 - d_3 - d_4)}. \tag{20}$$

The signs in this equation are arranged in accordance with the supposition that L_3 is greater than $L_1 + L_2 + 2M_{12}$. Other relative magnitudes will require other signs.

Method 19, Comparison of Self-Inductance with Capacity, Null Method. — The coil whose self-inductance is L is connected in one branch of the galvanometer circuit, according to the scheme indicated in Fig. 1. Non-inductive resistance is included in series with the coil. The condenser whose capacity is C is connected in parallel with any required portion of this resistance, by means of traveling plugs. (*a*) Balance the resistances for zero deflection, using steady current. (*b*) Shift the traveling plugs to obtain zero ballistic deflection when the commutator K is reversed. If R is the resistance then bridging the terminals of the condenser, the ratio of self-inductance to capacity is

$$\frac{L}{C} = R^2. \tag{21}$$

Method 20, Comparison of Self-Inductance with Capacity, Niven's Null Method.[1] — Branch circuits are made up between points A and B, including on one side a non-inductive resistance, one coil of the galvanometer and the inductance L, in order; on the other side a non-inductive resistance, the other coil of the galvanometer and a second non-inductive resistance. (*a*) Balance the resistances for zero deflection, using steady current. (*b*) Connect the condenser whose capacity is C, one terminal to a traveling plug which is placed at a point in the non-inductive resistance, in the branch in which L is found, near the galvanometer; the other terminal to a traveling plug which is joined to the opposing resistance at a point further from the galvanometer. Adjust the traveling plugs to obtain zero ballistic deflection of the needle of the galvanometer when the commutator K is reversed. If R_1 is the resistance from point A to the first plug, and R_2 is the resistance from A to the second plug, the required ratio is

$$\frac{L}{C} = R_1^2 - R_2^2. \tag{22}$$

Method 21, Comparison of Self-Inductance with Capacity, Deflection Method. — Connect the coil whose self-inductance is L according to the scheme indicated in Fig. 7. Capacity C is to be joined in parallel with either one of two equal resistances 1 and 2, each R ohms. (*a*) Balance the resistances for zero deflection, using steady current. (*b*) Measure the ballistic deflection d_1, resulting from reversal of the commutator K when the condenser is in the position 1. (*c*) Measure the ballistic deflection d_2, when the condenser is in

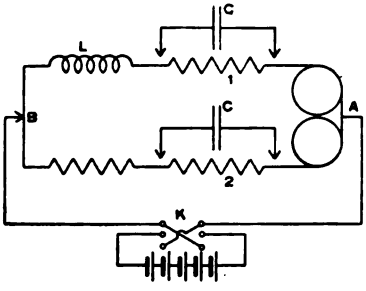

Fig. 7.

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[1] Phil. Mag. (5), Vol. 24, p. 231, 1887.

the position 2. The required ratio of self-inductance to capacity is

$$\frac{L}{C} = R^2 \cdot \frac{d_2 + d_1}{d_2 - d_1}. \qquad (23)$$

Method 22, Comparison of Mutual Inductance with Capacity, Null Method. — The two coils whose self-inductances are L_1 and L_2, and whose mutual inductance is M, are connected in series, their magnetic fields either coinciding in direction or opposed. The total inductance of the coils, $L_1 + L_2 \mp 2M$, is then compared with the capacity C by method 19. If R_1 is the resistance in parallel with the condenser, required for zero ballistic deflection when the inductance is $L_1 + L_2 + 2M$; and R_2 is the resistance when the inductance is $L_1 + L_2 - 2M$; the required ratio is

$$\frac{M}{C} = \frac{R_1^2 - R_2^2}{4}. \qquad (24)$$

Method 23, Comparison of Mutual Inductance with Capacity, Deflection Method. — The coils whose mutual inductance is M are connected in series and placed in the position occupied by the inductance L in Fig. 7. The capacity C is connected in parallel with either of the resistances 1 or 2, which need not be equal. (*a*) Balance the resistances for zero deflection of the needle of the galvanometer, using steady current. (*b*) Measure the ballistic deflection d_1, resulting from reversal of the commutator K, when the coils are connected for total inductance $L_1 + L_2 + 2M$, the condenser$_1$ being disconnected. (*c*) Measure the ballistic deflection d_2, resulting from reversal of the commutator when the total inductance is $L_1 + L_2 - 2M$, the condenser still disconnected. (*d*) Measure the ballistic deflection d_3, when the condenser is connected in parallel with resistance 1 and the total inductance is $L_1 + L_2 + 2M$. (*e*) Measure the ballistic deflection d_4, when the condenser is in parallel with resistance 2 and the total inductance is $L_1 + L_2 + 2M$. If R and R_2 are the magnitudes of the resistances 1 and 2, the required ratio of mutual inductance to capacity is

$$\frac{M}{C} = \frac{R_1^2 + R_2^2}{4} \cdot \frac{d_1 - d_2}{d_4 - d_3}. \qquad (25)$$

OTHER APPLICATIONS OF THE DIFFERENTIAL BALLISTIC GALVANOMETER.

In addition to the methods of measurement described in this paper, many of the published methods of determining inductance and capacity which make use of the Wheatstone network, may be carried out with the aid of the differential ballistic galvanometer. The Rayleigh-Maxwell method of measuring self-inductance may be taken as an example. Four resistances, three non-inductive and one containing the inductance to be determined, form a quadrilateral, whose diagonals are occupied by a battery and a galvanometer respectively. If the galvanometer is replaced by a short wire, and the coils of a differential galvanometer are included with two of the resistances of the quadrilateral, one each side of a junction with the short wire, the measurement of inductance may be made as usual, in terms of resistance, deflection and period of vibration of the needle of the galvanometer. When the resistance of the galvanometer is small, there is no apparent gain in the use of the differential arrangement. When its resistance is large, then for given resistances and battery power, nearly twice the ballistic deflection may be obtained with the differential galvanometer, that would result from the use of the same galvanometer, its coils connected in series and employed as a ballistic galvanometer of the ordinary type. When the inductance to be measured is small and the resistance associated with it is large, relatively large current must be used to secure ballistic deflections which can be measured. Under these circumstances there is difficulty in maintaining balance of resistances when steady current is flowing, because of unequal heating effects in different parts of the circuit. Lessening the current required to produce a given deflection, decreases the heat liberated in the circuit in proportion to the square of the current, and tends to obviate the difficulty described.

Comparing the Rayleigh-Maxwell method with method 10 of the list now offered, the latter method has the advantage of greater sensitiveness. This may be established by comparison of the expression for the discharge through the galvanometer in the former method, with equation (4) of this paper. It is assumed for this comparison that the same amount of wire is wound in a single coil, or differentially in two coils, and that the steady current flowing through the inductive resistance is the same in both methods. The advantage of greater sensitiveness, shared by other methods here described, increases in general with higher resistance of the galvanometer coils. The writer is convinced that partly because of greater simplicity of connections, leading to greater ease of manipulation, partly because of increased sensitiveness or smaller steady currents required for the same deflection of the galvanometer needle, the methods now presented will show some real gain in precision, over the methods which make use of the Wheatstone quadrilateral and a ballistic galvanometer of the ordinary type.

UNIVERSITY OF CALIFORNIA,
March, 1905.

MAGNETIC EFFECT OF ELECTRIC DISPLACEMENT.

By J. B. Whitehead.

Part I.

In two former papers[1] the writer described a series of experiments which were undertaken as a test of the validity of Maxwell's assumption of the presence of a magnetic effect accompanying an electric displacement in a dielectric. The results of the experiments have been shown by Kolacek[2] to be in accord with Maxwell's theory. From the symmetry of the Maxwell equations we must expect an electrical effect or force accompanying magnetic displacement (if we may use the analogous expression). Thus in the writer's experiments the resulting mechanical force acting on the dielectric was shown by Kolacek to be

$$\frac{K}{4\pi V}\frac{d}{dt}ZM;$$

where K is the dielectric constant, V the ratio of the two systems of units, Z the electric intensity in electrostatic and M the magnetic intensity in electromagnetic units. Since in the experiments both Z and M were periodic functions differing in phase by 90° the mean value of over a period the force was zero, and therefore there was no motion of the dielectric. This result then is a proof of the existence of the electric effect of the "magnetic displacement current," if the magnetic effect of electric displacement be granted. Evidence of the existence of the latter has recently been given by the work of Eichenwald,[3] although many other experimenters have sought it with negative results. It is therefore desirable that further evidence be had, and the present work was undertaken with the aim of observing the two effects independently.

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[1] Mag. Eff. of Elec. Disp. Report to Carnegie Institution, 1904, and Phys. Zeits., 4, 229, 1903; 5, 300, 1904.

[2] Phys. Zeits., 5, 45, 1904.

[3] Annalen der Physik, 6, 1903.

The following experiment was devised for showing directly the magnetic effect of electric displacement.

If a portion of dielectric be subjected to an alternating electric intensity, alternating displacement currents will be set up in the dielectric. If, now the dielectric be properly surrounded by a magnetic circuit, alternating magnetic induction will be set up therein, and if this circuit be wound with a number of turns of wire, an alternating E.M.F. will be induced therein, and this E.M.F. may set up a current. The value of the current may be calculated and measured. As constructed the dielectric was a cylinder of paraffin. The E.M.F. was applied to electrodes consisting of circular brass plates on the end faces of the cylinder. Concentric with the cyinder and surrounding it was the laminated magnetic circuit consisting of soft iron disks; the iron ring thus formed was wound with what may be called the secondary winding, in circuit with which the measuring instrument was connected.

Preliminary calculations indicated that the apparatus would have to be of large size, and also that means for measuring very small values of alternating current must be had, if the expected effect was to be detected.

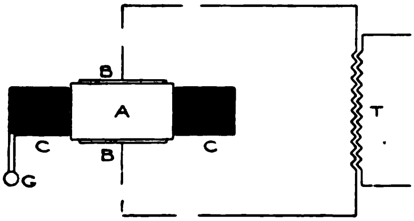

Fig. 1.

Consider the apparatus as shown in a diametral section in Fig. 1. A is the cylinder of dielectric, BB are the electrodes, CC the surrounding magnetic circuit. If E is the difference of potential between the electrodes, E/l is the electric intensity active on the dielectric, l being the length of the cylinder. The density of the displacement current is then

$$q = \frac{K}{4\pi l}\frac{dE}{dt}.$$

If $E = E_m \sin a$, $q = \frac{K}{4\pi l} E_m \frac{da}{dt} \cos a$; and since $\frac{da}{dt} = 2\pi N$

$$q = \frac{K}{4\pi l} E_m 2\pi N \cos a.$$

If a be the area of the circular section of the cylinder, the total current is

$$i = \frac{KE_m Na}{2l} \cos a,$$

if E is expressed in volts and i in amperes

$$i = \frac{KE_m Na 10^8}{2l(3 \times 10^{10})^2 \times 10^{-1}} \cos a.$$

In the experiments $K = 2$, $E_m = \sqrt{2} \cdot 25{,}000$, $N = 133$, and $a = \pi\ 19.25^2 = 1{,}164$ sq. cm.; $l = 20$ cm. The maximum value of the current is therefore

$$i = \frac{2 \times 25{,}000 \times 133 \times 1{,}164 \times 10^8 \times \sqrt{2}}{2 \times 9 \times 10^{19} \times 20} = 3.03 \times 10^{-4} \text{ amperes},$$

$$i\ (\textit{effective}) = 2.15 \times 10^{-4}.$$

The magnetic effect of this current in a surrounding magnetic circuit will depend on the distribution of the current in the dielectric. The most obvious assumption is that the effect is the same as though the current were all concentrated at the center, *i. e.*, on the axis of the cylinder. We may then calculate the magnetic intensity at any distance from this axis, assuming that the wires leading to the electrodes, and the dielectric are equivalent to a long straight conductor lying along the axis of the apparatus. The leading-in wires were accordingly long and straight. We have then:

Maximum value of H, the magnetic force at a radius of 20 cm. $= 2i/10 = 3.03 \times 10^{-6}$, at radius of 40 cm. $H = 1.51 \times 10^{-6}$. The magnetic circuit was composed of rings of annealed sheet armature iron, 41.4 cm. internal and 82.8 cm. external diameter. Built up and compressed the depth was 15.5 cm.; the cross section was thus 320 sq. cm. The weight was 900 lbs. The average value of H may then be taken as 2.26×10^{-6}. The wires leading to the electrodes continued straight away for 100 cm. on each side. They then turned through a right angle and were led parallel to each other to the transformer 5 meters away. The correction factor for this departure from the infinite straight conductor may readily be shown to be only $.09i/r$, for the magnetic force as calculated from the expression $H = 2i/r$; thus the average value is $H = 2.09i/r$. Using the values for i and r given above, the average value of H becomes 2.36×10^{-6}.

$$\therefore \text{Total Magnetic Induction} = 2.36 \times 10^{-6} \times \mu \times 320.$$

Data as to the permeability of soft iron in laminations at such low values of the magnetic intensity are meagre.

Values of μ for small magnetizing forces have been determined by Baur[1] and Lord Rayleigh.[2] The latter carried the field from 4×10^{-2} down to 4×10^{-5}, and showed that μ was constant throughout this region; there is nothing to indicate that it will change for values of H still nearer to O. This value for soft iron is 183, as obtained with constant magnetic force on bars. Ewing states that for laminated structures there is little if any viscosity, or lag, at small forces.

If we assume this value we have:

$$\text{Total Induction} = 2.36 \times 10^{-6} \times 320 \times 183 = 1.35 \times 10^{-1}.$$

A secondary winding consisting of 966 turns of No. 18 B. & S. wire completely surrounded the magnetic circuit. A similar winding of the same number of turns was afterward wound over this, the two coils beginning and ending at the same point. The E.M.F. induced in one of these windings is:

$$\begin{aligned} E &= 1.35 \times 10^{-1} \times \pi\sqrt{2} \times 133 \times 10^{-8} \times 966 \text{ volts,} \\ &= 7.8 \times 10^{-4} \text{ volts.} \end{aligned}$$

If we can measure a current due to this E.M.F. we have a test of the validity of the theory subject to the assumptions already stated. The Rubens Vibration galvanometer[3] was used as measuring instrument. Its principle is the adjustment of the tension of a stretched wire so that its natural frequency of oscillation is the same as that of the electric circuit. The wire carries a row of small magnets in suitable relation to poles carrying coils traversed by the current to be measured. The amplitude of the oscillation, observed by light reflected from a small mirror on the wire is a measure of the current. The instrument was obtained from W. Oehmke, Berlin, and was made from the specifications contained in the article already referred to. It was calibrated by the following method. A low value of alternating E.M.F. of the frequency to be used was impressed on a noninductive resistance of 2,000 ohms; connections were made at two points differing by 100 ohms, and between them the galvanometer, in series with a noninductive resistance of 10,000 to 100,000 ohms, was inserted. The galvanometer being tuned to synchronism for the frequency used, the widths to which a slit of light reflected from the mirror is spread out, corresponding to the various values of current, were read. The filament of an incandescent lamp was used as source, and the spreading of the image was measured on a scale; in the eyepiece of the telescope the scale could be read to tenths. The calibration curve, given by the accompanying table, covers the range of the experiments. The resistance of the instrument was 215 ohms.

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[1] Wied. Ann. XI., 1880, p. 399.

[2] Phil. Mag., March, 1887.

[3] Wied. Ann., No. 56, p. 27.

Amperes.	Deflections.	Amperes.	Deflections.
4×10^{-5}	4.2	3.3×10^{-6}	.6
2×10^{-6}	2.1	2.8×10^{-6}	.55
1×10^{-5}	1.2	2.5×10^{-6}	.5
6.6×10^{-6}	.95	2.2×10^{-6}	.45
5×10^{-6}	.8	2×10^{-6}	.4
4×10^{-6}	.7		

If now the instrument is connected with the secondary winding ($r = 13$ ohms) by the calculation above, the order of magnitude of the resulting current in it should be $(7.8 \times 10^{-4})/228 = 3.42 \times 10^{-6}$ amps.

The Experiments. — The source of current was an 8-pole single phase alternator giving approximately a sine curve of E.M.F. at 110 volts effective value. It was directly connected to a direct current motor, supplied from 110-volt mains. A heavy flywheel on the shaft and rheostats in the field and armature of the motor, controlled from the point of observation, resulted in a suitable constancy and control of the frequency. The alternator supplied the primary of a step up transformer of ratio 100/25,000, the high tension terminals being connected to the electrodes. The transformer was at 5 meters distance from the apparatus proper, the wires being parallel and 2.5 meters apart until they intersected the axis of the apparatus. The lower electrode supported the paraffin, and the upper rested on it. The galvanometer was near the magnetic circuit and suitable tests indicated that it was free from electromagnetic disturbances due to alternator, transformer, etc. A reversing switch was placed between the secondary winding and the galvanometer, also a single pole switch which opened one side of the circuit only. A small solenoid placed near the galvanometer, and supplied from the machine, served as a test for synchronism and constancy of conditions. The apparatus as described permits several variations of conditions, giving different values of the current to be expected in the galvanometer. Paraffin or air may be used as dielectric; the secondary coils may be used single, in series, or in parallel. Different values of voltage and frequency were not used, as spurious effects would also probably vary with these quantities.

A typical set of readings is given in the table.

Secondary Coils.	**Paraffin.**					**Air.**				
					Mean.					Mean.
Coil No. 1, No. 2 open.	.8	.8	.9	.8	.82	.6	.6	.6	.5	.57
Coil No. 1, No. 2 closed.	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
Coil No. 2, No. 1 open.	.8	.9	.9	.8	.85	.6	.6	.6	.6	.6
Coil No. 2, No. 1 closed.	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
Coils No. 1 and No. 2 in series.	1.3	1.3	1.3	1.4	1.32	.9	.9	.9	.8	.87
Coils No. 1 and No. 2 in parallel.	.7	.75	.8	.8	.76	.5	.5	.5	.6	.52

These readings were unchanged on reversal of galvanometer connections. Primary voltage 113. Frequency 130. The method of observing was as follows: By means of the rheostat in the motor field the speed was gradually brought to the desired frequency, this being indicated by the broadening of the image of the filament on the telescope scale. The machine was then allowed to run free, and the condition of perfect synchronism would hold for several seconds, often longer; it would then drop out for a few seconds and then return. The readings given represent, in each instance, the observations of at least three of these recurring periods of synchronism. Observations made on different days, the paraffin being removed for the air reading after each set, gave readings in good agreement with those in the table.

It will be noted that the values with air as dielectric are uniformly lower than those for paraffin, as is to be expected. They do not, however, differ in the ratio of the dielectric constants. In view of the uncertainty of the values of these constants at the frequency used, and of the uncertainty of the distribution of the field in the two cases, the discrepancy does not appear serious. More important, however, is the fact that the series arrangement of the two secondary coils does not result in a doubled value of the reading for either coil alone, although it is noticeably greater; a possible explanation lies in the arrangement of the windings of the two coils. As already stated, the two coils were wound in parallel in a single layer. Thus when connected in series half of the total induced E.M.F. existed between each pair of wires. This difference in potential would tend to upset the symmetrical and uniform oscillation of the electrostatic charges induced on the secondary winding, thus resulting in the equivalent of a current which would cause a second induced E.M.F. in the secondary winding. This would not occur in the parallel arrangement, and the readings conform to this view.

That these electrostatic charges introduce no error in the readings is indicated by the observations given in the tables for "closed" coils. The short circuiting of one coil always nullified the E.M.F. in the other. This shows that the current in the galvanometer circuit is electromagnetically induced and is not electrostatic in its origin. Aside from this the symmetrical form and arrangement of the apparatus gives no cause for an unsymmetrical oscillation of the induced charges.

Conclusion. — The calculated effect for one coil reduced to the conditions of the test, *i. e.*, 113 volts and 130 cycles, is 3.16×10^{-6} amps. The current corresponding to the mean values (.82) of the deflections for coil No. 1, as given by the calibration curve, is about 5.2×10^{-6}. The observed effect is thus of the same order of magnitude as that calculated; the uncertainty of the assumptions which have been made may well account for the difference in the numerical values.

Part II.

The following modification of the writer's earlier experiment[1] was suggested by Kolacek for showing the electric effect of magnetic displacement. Place the dielectric in a constant electric field and a magnetic field at right angles thereto; if the magnetic field be suddenly reversed we should according to Maxwell's theory expect an implusive force to act on the dielectric. For the expression for the force now becomes $K/4\pi VZ \, \partial/\partial t \, M$, since Z is a constant, *i. e.*, there is no electric displacement current. According to Kolacek this experiment also affords a test of the modifications of Maxwell's theory suggested by Lorentz. The former in expressing the value of the displacement current as $K/4\pi \, \partial Z/\partial t$ says nothing as to the mechanism in the dielectric; simply that the impression or relief of electric tension or polarization in a dielectric of specific inductive capacity K is equivalent in magnetic effect to current of density $K/4\pi \, (\partial Z/\partial t)$. Lorentz, however, assumes that the displacement current is made up of two parts, first the polarization of the ether, and second the displacements of atomic or ionic charges within the molecules of the dielectric; that these being actual motions of charges are equivalent to currents and that Maxwell's expression $K/4\pi \, (\partial Z/\partial t)$ is equivalent to $1/4\pi \, (K_e + \Sigma' c) \, \partial Z/\partial t$, where K_e is the value of K for the ether and $\Sigma' c$ is the summation of the molecular convection currents. This assumption admits the magnetic effect of electric displacement, but in the proposed experiment in which we should expect a deflection according to Maxwell, the electric field is constant, the convection currents are absent, and therefore according to Lorentz there would only be reaction on the ether which would cause no deflection of the matter of the dielectric.[2] This conclusion has been questioned by R. Gans[3] who concludes that according to Lorentz a deflection is to be expected, but that it would have a value $K - 1/K$ times that based on Maxwell's original theory.

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[1] Phys. Zeits., 4, 229, 1903.

[2] Kolacek, Phys. Zeits., 5, 455, 1904.

[3] Phys. Zeits., 5, 162, 1904; 5, 627, 1904.

A calculation of the magnitude of the impulsive force for a specific case indicated (as is shown below that) it would be so small that its effect would be difficult if not impossible to observe directly. Nevertheless it was decided to carry the experiment through with as favorable conditions as possible, in order to see how nearly a calculated effect might be approached by increasing as far as possible several factors.

Apparatus. — As dielectric a cube of rock salt 1 cm. on an edge was used. This was first suspended between two vertical parallel plates at different potentials; it was found that in this arrangement the dielectric had no equilibrium position owing to the irregular distribution of the field; the following arrangement was therefore adopted. The dielectric was attached to the center of a light glass rod, which was suspended by two silk fibers so as to lie along the axis of a circular coil. Two horizontal parallel brass plates were placed respectively above and below the dielectric, and being suitably supported and insulated constituted the electrodes. The dielectric was thus suspended in a magnetic field set up by the coil, and in an electric field set up by the electrodes at right angles to the magnetic field. The experiment then consists in reversing the magnetic field, the electric field being kept constant, and looking for a ballistic deflection of the block of dielectric. The force on the dielectric is as already stated, $K/4\pi Z\partial/\partial t M$, K being the dielectric constant, Z, the electric and M the magnetic intensity. These quantities were made as large as possible. Rock salt was chosen as the dielectric, the value for K being taken as 5. The coil for setting up the magnetic field consisted of 1,200 turns of No. 18 B. & S. wire; its internal diameter and its length were each 7.6 cm. The magnetic intensity at the center as measured by an exploring coil and alternating current was found to be 166 per ampere. In the experiments the current, limited by heating, was carried to 6.5 amperes; hence $M = 1{,}080$. Several plans for increasing the electric intensity in the dielectric were tried. The upper and lower faces of the dielectric were covered with metallic foil, a small strip extending from each parallel to the glass supporting arm. The electrodes described above being removed, very light hangers of fine wire were arranged to hang with small pressure against the strips projecting from the metal coatings of the dielectric faces, and so connect these coatings with the terminals of an induction machine. The slight pressure due to the hangers was in the same direction as the expected deflection. On charging, the little hangers were statically repelled, and if made heavier, the same effect set the dielectric in motion. After several modifications this method was abandoned as impracticable. Light wires from the metal coatings, dipping into cups of liquid conductor were then tried. In this case inequalities of surface tension prevented stationary conditions. The plan of suspending between horizontal electrodes was then adopted, the electrodes being brought as near together and the potential difference carried as high as possible, *i. e.*, until a greater value resulted in a discharge. The dielectric cube was 1 cm. on an edge, and the minimum distance between electrodes consistent with steady conditions was 2.2 cm. The potential difference was carried to 15,500 volts, as measured by the sparking distance between brass spheres, using the tables of Paschen[1] for calculation. The sensibility of the apparatus depends principally on the length of the suspending threads. They consisted of very fine silk fibers and their length was 112 cm. The whole apparatus was suitably enclosed, the suspending fibers occupying separate glass tubes.

We have then as values of the various quantities: Distance between electrodes 2.2 cm. Maximum potential difference at electrodes $E = 15{,}500$ volts. Maximum intensity of magnetic field $M = 1{,}080$. Length of suspension 112 cm. Dielectric cube 1 cm. on an edge. Mass of suspended system about 3 grams. We have then:

$$\text{Electric intensity in dielectric } Z = \frac{E}{ld + Kla} = \frac{15{,}500}{1 + 1.2K}.$$

If the magnetic field is reversed the consequent impulse on the dielectric is:

$$\int A\,dt = \frac{K}{4\pi V} Z \int dM$$

$$= \frac{5}{12.5 \times s \times 10^{10}} \cdot \frac{15{,}500 \times 10^{8}}{7} \cdot \frac{2{,}160}{3 \times 10^{10}}$$

$$= 2.1 \times 10^{-7} \text{ c.g.s.}$$

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[1] Wied. Ann., XXXVII., p. 79, 1889.

If we divide the moment of this impulse by the moment of inertia of the suspended system we have the consequent angular velocity of the dielectric cube. From this we derive its kinetic energy and hence the arc through which it will swing against the force of gravity. A calculation of this quantity gives for the deflection a magnitude of the order 10^{-6} cm., which not only explains the uniformly negative results of the experiments, but indicates that in this form the experiment suggested by Kolacek cannot be expected to give evidence on the questions at issue.

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THE INFRA-RED SPECTRUM OF CO_2 AND NITROGEN.

BY E. R. DREW.

THE present investigation consists chiefly of an attempt to determine the source of the band which the writer[1] found at 4.75 μ in the radiation from the positive column of a Geissler-tube discharge in air. I had thought it probable that the band was due to nitrogen, but Professor Warburg suggested that it might be due to CO_2, as it is in the neighborhood of the well-known band at 4.4 μ, and no special precautions had been taken to get rid of this persistent gas. Further, Paschen[2] found that the position of this band varies with the temperature, from 4.27 μ at 17° to 4.4 μ in the Bunsen flame. It was, therefore, of interest to see whether it would be still farther displaced, toward the longer waves, in the radiation from the Geissler tube, in which the relatively high optical efficiency points to emission under conditions which would correspond to exceedingly high temperatures in flames. The same reasoning would require the wave-length to become greater as the pressure of the gas in the tube decreases.

The results obtained are, briefly, that a tube filled with CO_2 shows a maximum at 4.67 μ when the pressure is 3 mm., and at 4.70 μ at 0.6 mm. — these being the extreme pressures which could be used. The much smaller band which occurs at 2.7 μ in the absorption spectrum of CO_2 at 17° also gave deflections which were unmistakable, but not large enough to locate it with certainty. Its approximate wave-length is 2.47 μ. The tube was then filled with air, and later with nitrogen, freed from CO_2, with which there was no evidence of CO_2 in the color of the discharge, or in the visible spectrum. There was then no trace of the small CO_2 band, but there was again a maximum at about 4.7 μ, which, however, showed no evidence of displacement with change of pressure.

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[1] PHYS. REV., XVII., p. 321, 1903.

[2] Wied. Ann., 53, p. 334, 1894.

Apparatus. — A mirror spectrometer with rock-salt prism was used, with the mirror-prism device of Wadsworth, it being convenient to keep the telescope and collimator tubes fixed. This allowed an approximately air-tight house to be built about the prism, in which drying material was kept. The prism surfaces thus remained in good condition throughout.

The vacuum-tube is shown in section in Fig. 1. The collimator slit, at *S*, was 0.35 mm. wide and 6 mm. long, cut in a piece of sheet aluminium, and placed 2 mm. behind a somewhat larger opening in the anode, also of aluminium. The constricted portion of the tube in front of the anode is of elliptical section, 3 x 8 mm., enlarging toward the cathode, which is an aluminium cylinder, entirely shielded from the slit by the shoulder of the tube. It was hoped by this means to secure the greatest possible intensity in the radiation passing through the slit. A serious disadvantage proved to be the fact that this intensity depended chiefly upon the distribution of current just in front of the anode, and this was liable to change at any time. A series of readings was often thus spoiled when half finished; and series of readings which were in themselves consistent, could seldom be compared with each other. The tube was set in the collimator tube so that the slit came in the proper position, the inner end closed by a fluorite plate and the outer by a rather rough plate of rock-salt, through which radiation from an outside source could be passed through the slit.

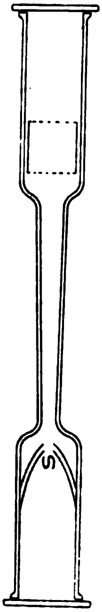

Fig. 1.

It was impossible, on account of magnetic disturbances, to use a thermopile as receiving instrument, so a radiometer was constructed. In an aluminium plate placed just inside the fluorite window, a slit exactly like the collimator slit allowed the radiation to fall upon one of the vanes. The whole inner face of this plate, including the slit, was covered by a thin plate of mica. The maximum elongation was reached in about 30 seconds, and the instrument was about twice as sensitive as the one used by the writer at Ithaca.

The chief difficulty in the investigation arose from the fact that it was necessary to use a form of Julius suspension for the radiometer, to free it from the tremors of the building. It was thus not a fixed part of the spectrometer, and its relative position varied slightly from time to time.

Current was obtained from a storage battery of 1,250 volts.

Observations. — The difficulty described above made necessary the adoption of a rather laborious method for taking observations. This consisted in simultaneously locating the maximum for the radiation from the discharge in the tube, and for that from the Bunsen flame, by reading a deflection first for the one and then for the other at nearly corresponding points on the two curves. The radiation from the flame passed through an aperture 4 mm. in diameter in a screen 30 cm. from the slit, reaching the latter through the rock-salt window on the outer end of the tube. The radiometer deflections were then of the same order of magnitude for the two sources.

The refractive indices given by Martens[1] were used to construct a calibration curve for the prism, of refracting angle 60° 9′. The measured angle between the *D*-line and the $4.4\,\mu$ maximum agreed with the curve to within the errors of the settings. The smallest vernier reading was 0.5′, corresponding to $0.066\,\mu$ in this part of the spectrum, so it was desirable to locate the maxima to within 0.1′ if possible.

When the two slits are equal and parallel, so that the image of one with monochromatic light falls exactly upon the other, the plotted deflections caused by a line or very narrow band will give an isosceles triangle. A series of careful tests with the Bunsen flame showed that these conditions were nearly enough fulfilled to justify the location of a maximum by the intersection of two straight lines drawn through the points representing three or four deflections on each side of the maximum. It was usually obvious that from one to three of the largest deflections did not belong to the triangle, so these were left out of account in the plotting. In one trial of the method, three sets of readings were made for the flame, two simultaneously, the third immediately after, and the extreme difference among the results for the position of the maximum was 0.07′.

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[1] Drude's Ann., 6, 623, 1901.

It is hardly necessary to reproduce all of the plots on which the results are based. Their character is well enough indicated by the samples given in Fig. 2. In each case the upper plot is for the flame, while the lower is for the gas used, as follows:

A. CO_2, pressure 0.6 mm. *C.* Air, pressure 0.6 mm.
B. " " 3.0 " *D.* " " 3.0 "

A represents one of the earlier series of readings taken, and is one of the poorest. In each plot the abscissas are circle readings in minutes of arc, the ordinates deflections in millimeters on a scale at 100 cm. The current in all cases was 0.01 ampere.

With CO_2 the pressure increases rapidly on first starting the current, on account of the decomposition of the gas into CO and O, which according to Collier[1] may amount to 65 per cent. After a few minutes a fairly steady condition is reached, and there is no further trouble.

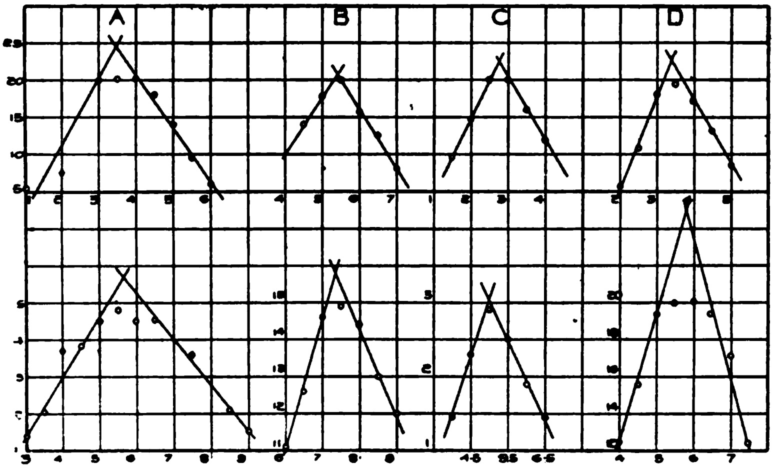

Fig. 2.

All of the gases used were dried by passing through strong H_2SO_4 and a long tube of P_2O_5. The air and nitrogen were freed from CO_2 by passing through a KOH tube. The gas was then pumped through the tube, while a current more than twice as strong as that used in the measurements was passed through it continuously for more than an hour, keeping the tube quite hot, until the discharge showed none of the characteristic color due to the carbon bands, and none of these were visible in the spectroscope. It was then thought hardly probable that the weaker current, which warmed the tube only slightly during the 30 seconds required for a deflection, would set free enough CO_2 from the tube walls or the electrodes to give any very strong radiation. The only prominent lines seen in the spectroscope were the red hydrogen, and a green line, probably that of mercury.

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[1] Jour. Chem. Soc., 465, 1063, 1901.

Nitrogen was prepared from sodium nitrite and ammonium sulphate, left standing over water for 24 hours, and passed through pyrogallic acid solution to remove traces of oxygen.

In Fig. 3 the lower plot shows the small CO_2 band, at 3 mm. pressure, its intensity being roughly 0.07 that of the large maximum. The upper dotted curve shows the deflections obtained in the same region with nitrogen, which shows no trace of the CO_2 band.

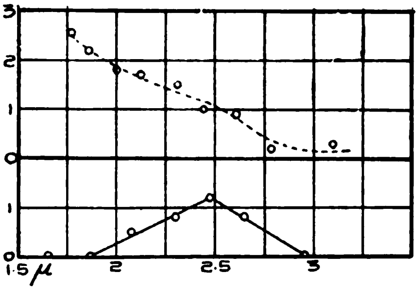

Fig. 3.

The numerical results given below express the distance of each maximum from that of the Bunsen flame in minutes of arc. The factor given after each result is a weight assigned to it in averaging, derived from the appearance of the plot, and the possible variation in the result caused by permissible variation in the plotting. The two starred results, which were obtained with nitrogen, agree so closely with those for air, that there seems no reason for treating them separately.

The mean results are below expressed in wave-lengths, assuming 4.40 μ for the flame maximum.

CO_2				Air.			
0.6 mm.		3.0 mm.		0.6 mm.		3.0 mm.	
2.20	4	2.25	4	2.33	3	2.35	8
2.21	1	1.96	2	2.25	10	2.19	5
2.52	1	1.99	10	2.11	9	*2.18	10
		2.04	8	2.18	4	*2.19	7
Mean 2.25		2.05		2.21		2.23	
4.697 μ		4.67 μ		4.692 μ		4.695 μ	

The radiation on its way through the spectrometer passes through nearly a meter of air, and suffers absorption by the CO_2 contained therein. The maximum for this absorption, according to Paschen, lies below 4.3 μ, so that its effect upon the location of the emission maxima will be small. It will also be very approximately the same in all cases, hence the apparent displacement of the CO_2 band with the pressure in the tube would not be affected.

On account of the previously mentioned fluctuations in intensity of the radiation passing through the slit it was impossible to make any definite comparison of the intensities of the maximum with the different gases used. There was no difference great enough to be certainly detected with the same current and pressure.

It was not thought worth while to try oxygen, since Ångström[1] found that its total radiation was not more than one tenth of that from nitrogen which was absorbed by his alum plate, and hence probably not more than one third of that given by this band alone.

It is possible that the maxima may be due to some impurity common to all the gases used; but it seems highly probable that those found with CO_2 are really due to that gas, while that found with air and nitrogen is not a CO_2 band.

From Paschen's results for the change in wave-length of the CO_2 band, from 4.27 μ at 17° to 4.4 μ in the Bunsen flame, the farther displacement to 4.7 μ in the vacuum tube seems reasonable on considering the character of the radiation, which here has a considerable portion within the visible spectrum, while in the flame it all lies comparatively far in the infra-red. An extrapolation of Paschen's results, which would be rather rash, would lead to the speculation that radiation similar to that of the vacuum tube might be gotten from CO_2 if it could be raised to a temperature of the order of 10,000°, provided that its properties were then the same as in the vacuum tube, which is not in the least likely.

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[1] Wied. Ann., 48, 509, 1893.

I take pleasure in expressing my thanks to Professor Warburg for placing at my disposal the facilities of the Physical Institute, and for many valuable suggestions during the investigation.

PHYSICAL INSTITUTE OF THE UNIVERSITY OF BERLIN,
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THE PHYSICAL REVIEW

ON BILLITZER'S METHOD FOR DETERMINING ABSOLUTE POTENTIAL DIFFERENCES.

By H. M. Goodwin and Robert B. Sosman.

IN an interesting article on Absolute Potential Measurements which appeared in Drude's Annalen,[1] in 1903, Mr. J. Billitzer describes three new experimental methods of determining the absolute potential between a metal and a liquid, and presents results obtained by these methods which, although sufficiently concordant among themselves, are completely at variance with those generally accepted, based upon the well-known surface tension phenomena. The magnitude of the discrepancy may be judged of by the fact that the value of the potential of a normal calomel electrode determined by the proposed methods is 0.74 volt above the value generally assumed. To explain this discrepancy the author suggests a modification of Helmholtz's double layer theory, namely that the opposed charges of a double layer are not, as heretofore assumed, equal, but that a positive or negative charge preponderates according to circumstances.

The theoretical importance of the questions thus raised by the results of this investigation seemed to us to make a further verification of the experiments on which the conclusions of the articles are based desirable. With this in view we undertook to repeat with as great care as possible the experiments described. As the exact conditions under which the experiments were carried out, particularly as regards the concentration of the solutions used, are stated very vaguely by the author, it was difficult or impossible to know just what the exact conditions were. We have attempted however to reproduce them as nearly as possible. It may be stated in advance that our experiments do not furnish a satisfactory confirmation of the results in question.

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[1] Ann. der Phys., 11, 902, 937, 1903.

THE PROPOSED METHODS.

The line of reasoning on which the proposed methods are based may be briefly stated as follows. If a minute metallic ball or particle be suspended in a liquid between which and the particle a difference of potential exists, there is formed at the surface of contact of the two a double layer (Helmholtz). The metal may possess a positive or negative charge with respect to the liquid depending upon the electrolytic solution pressure of the metal (Nernst), and on the concentration of the ions of the metal in the solution. If such a suspended ball or particle, supposed positively charged, be placed in the path of a strong potential gradient maintained from an external source by immersing two electrodes in the liquid, the positive charge on the particle will be attracted to the negative electrode or cathode, and the negative charge of the double layer in the liquid will tend to move in the opposite direction to the positive pole or anode. A motion of the particle in the direction of the current, *i. e.*, toward the cathode should result. If the polarity of the double layer be reversed, the motion should be in the opposite direction. If the potential between particle and liquid is zero, *i. e.*, the double layer disappears, there should be no motion. Electrostatic effects arising from induction due to unsymmetrical disposition of the ball with respect to the electrodes are of course supposed to be eliminated by observing with reversals of the polarity of the electrodes producing the field. Absence of motion of a particle or minute metallic ball suspended in a liquid through which a potential drop is maintained is taken therefore as indicating zero potential between the metal in question and the liquid, and if an auxiliary electrode of the same metal as the suspended particle be immersed in the liquid the potential between it and the liquid is also assumed zero. Such an electrode can then be used as a standard of reference in combination with other electrodes to determine the absolute potential difference between them and the solution in which they are immersed respectively.

The three following methods all based on this principle are proposed. The essential difference between them is the mode of observing the reversal point or disappearance of the double layer.

1. The deflection of a minute ball fused at the end of fine wire and suspended in a liquid by a quartz fiber is noted.

2. The direction of migration of a colloidal metallic suspension is noted.

3. The potential difference produced at the ends of a tube of liquid when a metallic suspension is allowed to fall through the liquid is noted.

In the experiments described by Billitzer all three methods lead to practically the same result, namely that a reversal of motion in case 1 and 2 and reversal of potential in case 3 occurs when the potential between the auxiliary electrode in the solution under investigation and a 0.1-normal calomel standard electrode is + 0.125 volt, or in other words assuming the P.D. at the auxiliary electrode to be zero, the P.D. (solution to metal) of a 0.1-calomel electrode is + 0.125 volt, *i. e.*, 0.74 volt greater than the value — 0.614 volt usually assumed.[1]

In the present paper we have repeated the experiments made by the first method. The experiments described under the second method have at the same time been made the subject of an investigation by Dr. J. C. Blake in connection with an extended research on colloids.[2] The results obtained by him failed completely to confirm those obtained by Billitzer, for it was found that the direction of migration of the metallic colloid (Bredig) could be varied at will by the addition of a greater or less amount of gelatine which it was necessary to add to prevent coagulation of the colloid when an electrolyte was added to the solution. Billitzer also used gelatine for this purpose in all of his experiments, but he fails to state in his article exactly how much was added. In his paper "ein Spur" is stated as being sufficient, while in a letter to Blake he states that "recht viel" was added.[1] The reversals observed by Billitzer in these experiments would seem therefore to be due to the variable gelatine concentration rather than to the disappearance of the double layer on the suspended particles, and hence his conclusions relative to the potential of reversal, so far as they rest on experiments based on the second method, do not appear to be warranted.

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[1] Billitzer erroneously adopts in his computation the P.D. of a normal calomel electrode instead of that of 0.1-normal electrode which he used in his experiments, *i. e.*, he bases his potentials on the value —.277 volt (normal hydrogen electrode = 0) instead of the correct value —.337 volt. The first of these values is moreover incorrect; the value should be taken as —.283 volt. See Wilsmore, Zeit. für Phys. Chem., 36, 91, 1901.

[2] Am. Journ. Chem. Soc., 26, 1378.

In view of the above results and those described below, the third method has not been further investigated.

APPARATUS AND METHOD.

The form of apparatus employed in our investigation was essentially that described by Billitzer. The following details are given for completeness and reference.

The Suspension. — A platinum wire 1.5 cm. long and 0.025 mm. in diameter with one end fused to a minute sphere was attached to a quartz fiber 26 cm. long by means of a bit of sealing wax. The fiber was suspended by means of a small loop of wire attached to its upper end from a hook of fine wire sealed into a glass tube. This tube could be raised or lowered through a cork which fitted the upper end of a glass guard tube to protect the fiber from air currents. The guard tube was 2.5 cm. in diameter and 35 cm. long. The lower end was drawn down and flared at the bottom as shown in Fig. 1.

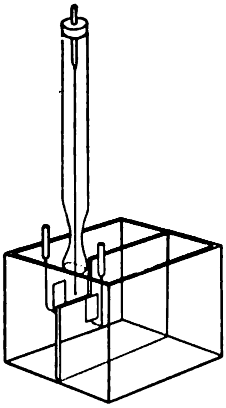

Fig. 1.

The Electrodes. — The electrodes to which the 110-volt or 220-volt circuit was applied to produce a potential gradient through the liquid in which the wire was suspended were of platinum foil 4 mm. × 8 mm. to which platinum wires were welded and sealed into glass tubes, contacts being made in the tube by means of mercury.

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[1] Journ. Amer. Chem. Soc., 26, 1378.

Two auxiliary platinum electrodes for measuring the potential of the liquid were used, one platinized and the other smooth. These were each 0.5 cm. × 1.0 cm.

The Vessel. — The vessel for containing the liquid was a cubical glass cell 5 × 5 × 5 cm. To concentrate the potential gradient at the suspended ball a glass partition was introduced as shown in Fig. 1. The opening in which the suspension hung was about 1 × 2 cm. The electrodes were placed one on each side of this partition. The whole vessel could be set into a beaker, the top of which was hermetically sealed by a paraffine cover through which the guard tube, electrodes, siphon and auxiliary tubes for withdrawing and admitting gases other than air were sealed. This permitted working in an atmosphere of hydrogen, carbon dioxide, etc.

Mounting. — With so delicate a suspension as that employed, the effect of mechanical jar had to be eliminated as far as possible. For this purpose the apparatus was set up on a brick and masonary pier free from the walls and floor of the building but still far from steady owing to heavy traffic in the street. On this was placed a slate block 51 × 51 × 15 cm. resting on hair felt, and on the slate block was placed a massive iron block 30 × 30 × 15 cm. The best results were obtained by supporting the iron block on three rubber stoppers placed at the vertices of an equilateral triangle. All of the apparatus was mounted on the iron block with the exception of the microscope which rested on the slate block, to permit adjustment without jarring the suspension and liquid. Even with this arrangement occasional vibrations were noticeable, but these were so small as not seriously to interfere with the observations.

Potential Measuring Apparatus. — For measuring the potential of the auxiliary electrodes against a 0.1-normal calomel electrode, the usual Poggendorff compensation method was used with a Lippmann electrometer sensitive to 0.001 volt as indicating instrument. The bridge constant was determined before each set of measurements by means of a Weston cadmium cell whose electromotive force determined against the laboratory standard Clark cell was found to be 1.020 volts.

The liquid in the cubical-shaped cell described above was connected with a 0.1-normal calomel electrode through an intermediate vessel containing 0.1-normal potassium chloride. Connection was made by means of a siphon containing 0.1-normal potassium chloride

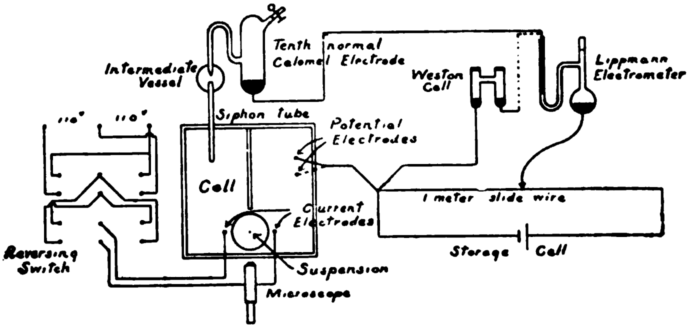

Fig. 2.

solution gelatinized by a little agar-agar. The complete arrangement of the apparatus is shown in Fig. 2.

Experimental Results.

We first made a number of preliminary qualitative experiments with the substances examined by Billitzer. The results agreed in the main with his, although there were several notable exceptions as will be seen from Table I.

Table I.

Qualitative Experiments.

Substance.	Billitzer. Charge of Pt. vs. Solution.	Goodwin & Sosman. Charge of Pt. vs. Solution.	Remarks.
Air.	—	—	
Distilled water.	—	—	
Water + trace NaCl.	—	—	KCl added instead of NaCl.
" + " acid.	—	—	HCl added.
" + Br.	—	—	
Acetone.	—	+	
Ethyl alcohol.	+	—	No deflection observed at first.
Formaldehyde.	+	+	
Hydrogen peroxide (40 per cent.).	+	—	2 per cent. was found to evolve too much gas for observation.
Ether.	+	+	
Chloroform.	+	+	No deflection at first.

A disagreement between our results and Billitzer's, which numerous repetitions of the experiment failed to remove, was found in the sign of the deflections in the case of acetone, ethyl alcohol and hydrogen peroxide. We were first inclined to attribute the disagreement to possible differences or impurities in the solutions, and proceeded at once to quantitative measurements in which the concentrations of our solutions were definitely known.

The first solutions thus investigated were mixtures of alcohol and water as the concentrations used by Billitzer were definitely stated for this particular case, and an exact repetition of the experiments seemed possible. The solutions used in our experiments were made up from 96 per cent. alcohol, while Billitzer states 94 per cent. as the strength used by him. Three concentrations were studied, 96, 81 and 32 per cent. respectively, thus covering the extreme range of concentrations previously investigated. Our results together with the corresponding ones obtained by Billitzer are given in Table II. In this and the following tables a negative deflection signifies that the motion was towards the anode, *i. e.*, the suspended wire was negatively charged with respect to the solution. The "deflections" are expressed in arbitrary divisions of the filar micrometer, their sign only being significant.

TABLE II.

Alcoholic-Aqueous Solutions.

Goodwin & Sosman.						**Billitzer.**		
Per Cent. Concentration.	**E. M. F.**	**Deflection.**	**Platinized Pt. vs. 0.1 Normal Electrode.**	**Polished Pt. vs. 0.1 Normal Electrode.**	**Fine Pt. Wire vs. 0.1 Normal Electrode.**	**Per Cent. Concentration.**	**Platinized Electrodes vs. 0.1 Normal Electrode.**	**Deflection.**
96	220	−2 to −3.	+0.050		+0.07	94	+0.155	+
96	220	−1.0	+0.003	+0.15		85	+0.15	+
81	220	−0.3 to −1.0	+0.037		+0.12	70	?	?
32	220	−3.5 to −4.0	+0.086	+0.10	+0.14	31	+0.139	—

The observations were taken after the lapse of one half hour to an hour to allow an equilibrium condition to be established between electrodes and solution. The variable values of the "deflection" are the result of a new vertical or lateral adjustment of the position of the suspended wire between the polarizing electrodes. It is to be noted that no positive deflection could be obtained even in 96 per cent. alcohol although Billitzer's results showed such deflections to occur in 78 per cent. alcohol and even 70 per cent. solutions. Moreover the potentials of the three types of auxiliary electrodes used, namely, platinized platinum, smooth platinum and wire similar to the suspended wire, showed no satisfactory agreement either with Billitzer's corresponding values or with each other. Results obtained with the platinum wire agreed on the whole best with Billitzer's. As to the best form of auxiliary electrode to use and the probable cause of the above discrepancies reference will be made later.

The power which alcohol possesses of reversing the potential of a platinum electrode as observed by Billitzer, is explained by an auto-oxidation by which hydrogen peroxide is formed. Hence it was concluded that addition of small amounts of this latter substance should also have the power of reversing the potential of platinum in acid solution. This prediction was borne out by Billitzer's results, a reversal occurring as before at approximately 0.125 volt, *i. e.*, platinized platinum *vs.* 0.1-normal calomel electrode. We repeated these experiments varying the concentration of hydrogen peroxide from 0.2 per cent. to 0.001 per cent., but obtained in every case a negative deflection. The condition of our solutions must have been essentially the same as Billitzer's, as the potential of the platinized electrode *vs.* 0.1-normal calomel electrode agreed fairly well with that found by him. It may be noted here that hydrogen peroxide was one of the substances which in our preliminary experiments was found to give results disagreeing with the published ones. Billitzer obtained a positive deflection in 40 per cent. hydrogen peroxide. We were unable, however, to obtain reliable deflections with even a 2 per cent. solution on account of the violent disturbances in the liquid arising from the decomposition of hydrogen peroxide in the presence of platinum. Our results are given in Table III. together with Billitzer's first series with hydrogen peroxide for comparison. The concentrations in his experiments were not stated.

As an example of a strong reducting agent capable of effecting a potential reversal, formaldehyde was found by Billitzer to reverse the deflection when the platinum potential *vs.* 0.1 normal calomel electrode was as before 0.125 volt. As no statement is given to in-

TABLE III.

Hydrogen-peroxide Solutions.

Goodwin & Sosman.					Billitzer.	
Concentration in Per Cent.	E.M.F.	Deflection.	Platinized Pt. vs. 0.1-Normal Calomel Electrode.	Smooth Pt. vs. 0.1-Normal Calomel Electrode.	Deflection.	Platinized Pt. vs. 0.1 Normal Electrode.
0.2	220	−1.0 to −1.5	+0.29		+	+0.4
0.1	220	−5.0 to −6.0	+0.28	+0.28	+	+0.3
0.02	220	−6.0	+0.23		+	+0.2
0.004	110	−2.5	+0.20		+	+0.15
0.001	220	−3.5	+0.19	+0.20	?	+0.12
					—	+0.10
					—	+0.08

dicate whether weak or strong solutions of the substance were used we extended a series of measurements from a 40 per cent. to a 0.04 per cent. solution. In this case we were able to detect a reversal in the deflection in passing from a 10 per cent. to a 36 per cent. solution. The reversal potential however did not check Billitzer's, as will be seen from the results given in Table IV.

TABLE IV.

Formaldehyde Solutions.

Goodwin & Sosman.					Billitzer.	
Concentration in Per Cent.	E. M. F.	Deflection.	Platinized Pt. vs. 0.1-Calomel Electrode.	Smooth Pt. vs. 0.1-Calomel Electrode.	Deflection.	Platinized Pt. vs. 0.1-Normal Electrode.
40	220	0 to +0.3	−0.02	+0.06	+	+0.17
36	220	+0.3	−0.03	+0.04	+	+0.15
36	220	+0.2	+0.02	+0.07	+	+0.14
10	110	−1.5 to −2.0	−0.04		+(?)	+0.13
10	220	−2.5	−0.04		—	+0.12
2	220	−2	−0.06	+0.06	—	+0.11
0.4	110	−1.5 to −2	−0.10	+0.01	—	+0.10
0.2	110	−1.0 to −1.5	−0.07	+0.03	—	+0.09
0.08	110	−2.0	+0.02	+0.04		
0.04	110	−4. to −5.	+0.01	+0.07		

Finally we repeated the series of experiments in which the variation of the reduction potential of a solution was varied between wide limits by changing the relative concentration of ferrous and ferric ions in the solution. Billitzer found that by varying the relative concentration of these ions a reversal of the deflection of his test electrode occurred again at the characteristic potential between 0.10 and 0.13 volt. We did our best to check these results but without success. Our only guide for duplicating the concentration used was the statement that "die Koncentration der ursprünglichen Lösung wurde in verschiedenen Fällen verschieden, immer jedoch sehr klein gewählt." Billitzer used ferrous and ferric sulphates in his experiments; we used ferric chloride and ferrous sulphate.

TABLE V.

Ferrous and Ferric Salt Solutions. ($Fe_2Cl + FeSO_4$) *in Various Proportions.*

Goodwin & Sosman.						Billitzer.	
Concentration in Per Cent.		E.M.F.	Deflection.	Platinized Pt. vs. 0.1-Calomel Electrode.	Smooth Pt. vs. 0.1-Calomel Electrode.	Deflection.	Platinized Pt. vs. 0.1-Normal Calomel Electrode.
$FeCl_3$.	$FeSO_4$.						
0.001	0	220	0	+0.36	+0.41	+	+0.16
		110	−1.5			+	+0.15
		220	−3.0			+	+0.14
0.001	0.02	220	−2.5	+0.32		+	+0.13
0.001	0.03	220	−1.0	+0.315		(very. weak.)	+0.125
0.001	0.05	220	uncertain because of electrolysis.	+0.23		—	+0.10
						—	+0.09
0.05	0	220	uncertain because of electrolysis.	+0.50	+0.46		
0.035	0	220	uncertain because of electrolysis.	+0.49			
0.035	0	220	uncertain because of electrolysis.	+0.43			
0.001	0	220	negative	+0.38	+0.29		
0	0.1	220	electrolysis.	+0.27	+0.25		

In these experiments reliable deflections could be obtained only in the very dilute solutions on account of electrolysis. Whether the solution contained ferrous or ferric ions the platinum suspension showed deflections indicating the metal to be negatively charged in all cases. The auxiliary platinum electrode was under the same conditions always positively charged referred to Ostwald's zero.

MERCURY AND SILVER ELECTRODES.

In the above experiments platinum is to be regarded as an oxidation or reduction electrode. Among other metals whose electrolytic solution pressure is such that a reversal of their potential with respect to a solution can be effected by varying the ionic concentration of the solution, may be mentioned mercury and silver. These metals were both tried by Billitzer, the former as amalgamated fine platinum wire, and the latter in the form of very fine silver wire. Auxiliary electrodes of the pure metals were used for measuring the potential of the solutions against a 0.1-normal calomel electrode as before.

We tried both of these metals but obtained a reversal only with mercury. A reversal was observed by Billitzer with mercury in mercuric nitrate, in one experiment only.

In these experiments the suspended platinum wire ball was amalgamated by being placed as cathode in a solution of mercuric nitrate acidulated with nitric acid. The auxiliary potential electrode of platinum was similarly amalgamated. After amalgamation the wire showed numerous swellings along its length about 0.04 mm. in diameter, the wire being 0.025 mm. in diameter. The strongest mercuric nitrate solution used in the following measurements was 2.5 per cent. acidulated with six drops of nitric acid in 200 c.c. A solution of 0.1-normal potassium nitrate was used in the siphon to connect with the calomel electrode. The results are given in Table VI.

TABLE VI.

Mercury in mercuric nitrate solutions.

Concentration in Per Cent.	E.M.F.	Deflection.	Amalgamated Pt. vs. 0.1-Normal Calomel Electrode	Remarks.
2.5	110	+1.5 to +4	+0.405	No deflection at first.
1.25	110	+2.5	+0.403	" " "
0.13	110	+0.3 to +0.4	+0.385	
0.025	110	−0.4	+0.364	
	220	−0.4		
0.013	220	−1.5	+0.350	

It is to be noted that the reversal potential (between + 0.36 and + 0.39 volt) does not agree with Billitzer's + 0.125 value.

In the case of silver Billitzer could get no reversal by diluting a silver nitrate solution. The reversals all indicated the silver was positively charged *vs.* the solution. By the addition of potassium cyanide the concentration of silver ions can be almost indefinitely diminished and it is well known that the metal becomes negatively charged with respect to such a solution. Billitzer observed by his second method (direction of migration of colloids) that addition of potassium cyanide produced a reversal when the auxiliary electrode indicated a potential of between + 0.11 and + 0.16 volts *vs.* 0.1-normal electrode. We tried the experiment of noting the deflection of a very fine silver wire 0.043 mm. diameter suspended as before by a quartz fiber in an excessively dilute silver nitrate solution to which potassium cyanide was added. No trustworthy observations could be obtained at concentrations greater than about 0.0005 normal on account of electrolysis. As will be seen in Table VII., deflections were always negative even when the auxiliary silver electrode changed in potential from + 0.27 volt to — 0.30 volt *vs.* the 0.1-normal calomel standard. In silver nitrate alone we have certainly every reason to regard silver as positive *vs.* the solution, yet the sign of the deflections observed, if they are determined by the charge alone, would indicate the contrary.

TABLE VII.

Silver in silver nitrate + potassium cyanide.

Concentration in Mols. $AgNO_3$.	E.M.F.	Deflection.	Ag. Electrode vs. 0.1-Normal Calomel.	Remarks.
0.01	110	uncertain	+0.35	Electrolysis.
0.005	110	"	+0.33	"
0.0005	110	−1	+0.27	
	220	−1.5+	+0.27	
0.0001	220	−0.5	−0.30	.01-Normal $AgNO_3$ ppt. and redissolved in KCN and diluted ten times.

DISCUSSION.

A consideration of the preceding results show that:

First: The phenomenon in question, *i. e.*, of the reversal in deflection of the suspended wire does not appear to be general, but occurs only in exceptional cases. The general phenomenon would seem to be a motion of the suspended metal towards the *anode*.

Second: The reversal phenomenon does not appear to stand in any definite relation to the potential between the auxiliary electrode and the solution, the characteristic reversal potential of + 0.125 volt (platinum *vs.* 0.1-normal calomel electrode) found by Billitzer being in no case observed.

These two experimental facts seem to us to be reasonably well established by our experiments. We do not attempt to offer an explanation for the remarkably concordant results of Billitzer leading to entirely contrary conclusions. It is possible that some essential condition was observed in his work not sufficiently stated in his article to enable us to duplicate it in our experiment. If so we trust that it will be more clearly pointed out. Attention may be called, however, to several factors which impressed themselves upon us in the course of our work, which have a direct bearing on the phenomenon under discussion and which may lie at the foundation of the results observed.

Effect of Electrode Surface.

Does the auxiliary electrode indicate the same potential as that existing between the fine suspended wire and the same liquid? This is evidently a fundamental question as the interpretation of all results obtained by Billitzer rests on the assumption that the two are identical.

We carried out several experiments to test this point by comparing against a 0.1-normal calomel electrode the potential drop between a platinized electrode, a polished electrode and an electrode consisting of a fine wire used for the suspension. It might be expected that since the last is smooth wire with a ball fused at the end, it would comport itself electrometrically more nearly like the polished platinum electrode than the platinized electrode. It was found that potential measurements with such extremely fine wire electrodes and even with electrodes consisting of a bunch of such wires were difficult to make and rather uncertain in their results. The following figures show that the potential of a fine wire electrode and a platinized electrode in the same liquid may differ by several hundredths of a volt, the former being always higher.

Solution.	**Wire.**	**Platinized.**	**Polished.**
Formaldehyde.	+0.02	−0.064	+0.059
"	+0.10	+0.019	+0.041
Alcohol-water.	+0.07	+0.050	
"	+0.12	+0.037	
"	+0.14	+0.086	+0.100

Polished electrodes were found to be far less certain in their behavior than platinized electrodes, as was to be expected, and it might be fairly assumed that the wire electrodes would show similar irregularities. Platinized electrodes, on the other hand, when properly prepared by treating as cathode in dilute sulphuric acid to reduce and remove residues of the platinizing liquid (Ostwald), then washed in boiling water, gently heated and finally allowed to stand in distilled water, always gave concordant results among themselves.

Effect of Time on Potential Equilibrium. — A very marked effect of time on the potential of the auxiliary electrode was noted in some cases which was different for platinized and unplatinized electrodes. This was most marked in the case of formaldehyde solutions, and was noticeable in all other solutions except those of hydrogen peroxide and mercuric nitrate.

A gradual change in the solution may account in part for the progressive rise in potential observed: the point we wish to make however is, that the time required to reach equilibrium was much greater in the case of the platinized than in the case of the unplatinized electrode, and if the unplatinized suspended wire comports itself like the polished potential electrode the same kind of uncertainty in its indications as to deflections would result.

The cause of the gradual rise of potential of the auxiliary electrode potential, observed in distilled water was also investigated. The potential was lower in freshly boiled water than in water which had stood some time in air: the effect was therefore ascribed at first to dissolved oxygen, but when pure air was passed through carefully boiled water to resaturate it, the potential fell instead of rising. This suggested at once that carbon dioxide caused the change. Carbon dioxide from the lungs was passed through the water, and the potential rose; this carbon dioxide was then washed out by a current of pure air, and the potential fell to the value first obtained in air-washed water. Saturation of the water with pure carbon dioxide brought the potential up somewhat above that obtained in water which had stood in contact with air. Tory and Barnes[1] have observed such an effect with platinum, and ascribed it to air; it may be possible to explain their results by the presence of carbon dioxide.

Effect of Liquid Junction. — Of minor importance in the present investigation is the value of the potential difference arising at the junction of the 0.1-normal electrode and liquid under investigation. This is at best uncertain in experiments like the above, and although in many cases it is probably small owing to the nearly equal migration velocities of potassium and chlorine ions, yet with the somewhat complicated nature of the solutions and solvents used and their extreme dilution it is possible that it may attain a very appreciable value.

Effect of Dissolved Gases on the Sign of the Deflection.

We would like to point out one other factor which seems to us of much greater importance on the phenomenon in question than any of the preceding, and one which apparently has not been considered by Billitzer. We refer to the phenomenon described and investigated in 1861 by Quincke,[2] who found that minute bubbles of hydrogen, oxygen and air act exactly like solid particles when suspended in a liquid and *migrated towards the anode* when a current was passed through an aqueous solution containing them. In turpentine, however, he found that all substances which he investigated (except sulphur) migrated *positively, i. e.,* towards the cathode. Now it was frequently observed in our experiments that no deflection was produced at the first instant the voltage was applied. After visible electrolysis had taken place and minute bubbles appeared in the liquid, a deflection of the wire became evident and the deflection was always towards the anode. This seems to us significant, for although it is true that deflections were repeatedly observed at the instant the current was established and when no bubbles were visible on the end of the suspended wire, yet is quite conceivable, and indeed probable, that in the process of immersing the wire in the liquid from the air, very minute particles of air might remain attached to it, or might separate out on it from the liquid. The following experiment in the light of Quincke's results seem to bear out the above hypothesis. The platinum wire was suspended in turpentine and deflections observed with 220 volts applied. They were unmistakably positive. The resistance of the cell was so high that the current was less than 0.00001 ampere. In distilled water saturated with pure hydrogen, the deflection was distinctly negative. The presence of minute, even invisible, bubbles of gas on the suspended electrode which may arise from gases in the solution, from the air or from electrolysis, seems therefore to offer a very plausible explanation of the results observed.

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[1] Trans. Amer. Electrochem. Soc., 3, 95, 1905.

[2] Pogg. Ann., 113, 565, 1861.

Another factor which may also have at least a secondary influence on the deflections, is the possible motion of the liquid surface under the action of the applied voltage.[1] Such a motion of the surface was frequently noticed on closing the circuit, when the microscope happened to be focused so that the surface was in the field of view. Since a difference of potential exists between a liquid surface and the gas above it, such a motion does not seem *a priori* unlikely. This phenomenon is worthy of further investigation.

CONCLUSION.

The present investigation was undertaken in order to obtain a confirmation of Billitzer's results on absolute potentials by the method of deflections of a minute metallic electrode suspended in various solutions, under the influence of an electric current. The results obtained have failed completely to confirm the measurements obtained by him, and we are forced to the conclusion that the method proposed is not to be relied upon for the purpose for which it was developed. This conclusion is further strengthened by the results obtained by Blake on the migration of colloids, who has also failed to confirm Billitzer's measurements using the colloid method.

So far as our experiments go, it would seem that most of the phenomena observed may be explained on the assumption of the negative migration of gaseous particles in the liquid, as first demonstrated by Quincke in 1861.

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[1] F. B. Kendrick, Zeitschr. f. Physikal. Chem., 19, 625, 1896.

We believe therefore that the results obtained by Billitzer by the above described method afford as yet no sufficient grounds for rejecting the generally adopted values for the potential of the normal (or tenth normal) calomel electrode.

Since the above work was completed two other articles[1] have appeared by the same author in which he has determined absolute potentials by investigating the phenomena of concentration changes produced by the dropping electrodes first studied by Palmaer, and by a modification of Pellat's surface tension method. As the results obtained by both of these methods confirm approximately the author's previous results, a description of the precise conditions under which the former experiments were carried out seems all the more desirable.

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[1] Zeitsch. für Phys. Chem., **48**, 513 and 542, 1904.

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ON THE DISTRIBUTION OF ENERGY IN THE VISIBLE SPECTRUM.

By Edward L. Nichols.

THE direct determination of the distribution of energy in the visible spectrum of incandescent bodies is a somewhat difficult matter. Even with the most sensitive forms of linear bolometer or with the radiometer the deflections obtained by exploring the spectrum of artificial light sources are very small excepting in the red. The proper correction of this portion of the observed curve for slit width is likewise a matter of some uncertainty. The visible spectrum of sunlight, it is true, is of sufficient strength to admit of direct measurement and the spectrum of the electric arc affords easily measurable intensities; but the distribution of energy in the former is so seriously affected by varying atmospheric absorption as to render the sun worthless as a source of comparison in spectrophotometric work and the fluctuations in the brightness of the arc are also very great.

It is possible with an exceedingly sensitive radiometer to explore the visible spectrum of an artificial source of light such as the acetylene flame up to about .45 μ and I have been in possession for some time of a collection of data for this source of light obtained from measurements by G. W. Stewart and by Mr. W. W. Coblentz. Given such a curve, one can compute the curves of distribution for all spectra which have been compared with the acetylene flame by means of the spectrophotometer; but I have hitherto postponed these computations through a feeling of distrust in the accuracy of the corrections for slit width.

Knut Ångström,[1] in a recent paper, has published a curve of the distribution of intensities in the visible spectrum of the Hefner lamp. Ångström's values were obtained by an indirect method based upon Wien's equation

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[1] Ångström, Physical Review, Vol. XVII., p. 302; also Royal Society, Upsala 3d series, Vol. XX., 1904.

$$I_\lambda = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}}$$

In his measurements he avoids the difficulty arising from the very feeble intensities of the visible spectrum of this source of light by measuring the quantity

$$L_\lambda = \int_0^\lambda I_\lambda d\lambda = C_1 \int_0^\lambda \lambda^{-5} e^{-\frac{C_2}{\lambda T}}$$

where L_λ is the entire radiation lying between 0 and λ. The constants C_1 and C_2/T were determined by a series of such measurements and the value of the intensity of each wave length of the spectrum was then computed.

If we know the relative intensities of the spectra of the Hefner lamp and of the acetylene flame, and these are readily obtained by means of the spectrophotometer, the curve for the distribution of intensities of the acetylene flame may be deduced from Ångström's values for the Hefner lamp. I have recently shown[1] that the curve thus obtained is essentially identical with that obtained by the direct exploration of the spectrum of the latter source, to which reference has already been made.

The agreement of these results greatly strengthens our confidence in the validity of both and renders it desirable to compute the corresponding curves for the numerous sources of light of which we already possess spectrophotometric comparisons either with the Hefner lamp or with the acetylene flame. Materials for such computations are sufficiently abundant. We have, for example, the series of spectrophotometric comparisons of the Hefner flame with petroleum flames, gas flames, the light of the Welsbach mantel, the zircon light, daylight and sunlight made by Koettgen[2] and numerous similar comparisons of light sources with the acetylene flame, made from time to time in the Physical Laboratory of Cornell University. It is with the results of computations made upon such data that the present paper deals.

Ångström, in the paper already cited, determined by means of his compensated pyrheliometer the heat in calories per second received by a surface of 1 sq. cm. at meters distance from the Hefner flame. If the various curves for the distribution of energy in the visible spectrum of light sources are plotted to the same scale as

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[1] Nichols' Standards of Light, Proc. of International Elec. Congress of St. Louis, 1904

[2] Koettgen, Wied. Ann., 53, p. 793.

Table I.

Distribution of intensities in spectra of Hefner and C_2H_2 flames.

Wave-lengths.	Hefner.	Acetylene.	Wave-lengths.	Hefner.	Acetylene.
	Intensities from Ångström's Curve.	Intensity by Radiometer.		Intensities from Ångström's Curve.	Intensity by Radiometer.
.46	0.22	0.39	.62	5.40	4.86
.48	0.47	0.65	.64	7.00	5.88
.50	0.82	0.88	.66	8.60	6.61
.52	1.20	1.33	.68	10.55	8.10
.54	1.65	1.80	.70	12.60	9.65
.56	2.26	2.42	.72	15.10	11.40
.58	3.30	3.08	.74	17.80	12.90
.60	4.20	3.97			

Ångström's curve for the Hefner flame, with ordinates so chosen as to represent in each case a source of unit intensity, the areas of these curves would give the luminous energy received from each source in unit time per square centimeter of surface when the illumination is one lux. It was shown many years ago by Crova that the intensity of the yellow of the spectrum is proportional to the candle power of the source. This relation, which one would expect to find approximately true on account of the high luminosity of that portion of the spectrum, one can readily verify by means of the spectrophotometer. I have accordingly reduced the various curves to be considered to this unit intensity by making the ordinate for wave-length .590 μ equal in every case to that of Ång-

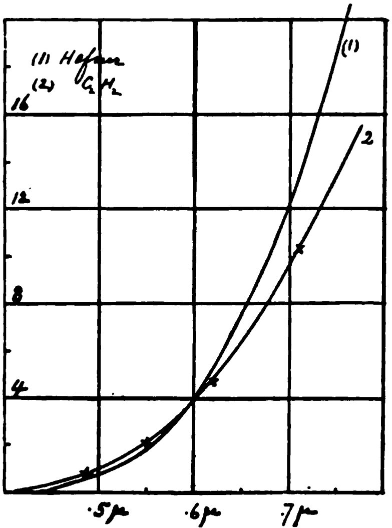

Fig. 1.

ström's curve for the Hefner flame. Ångström's curve and the corresponding curve for the acetylene flame, which are the reference curves for the reduction of the spectrometric data to be employed, are shown in Fig. 1 and the numerical data are given in Table I. Curve 2 in that figure is from direct determinations of the visible spectrum of the acetylene flame made with the radiometer, while the crosses (×) show the values for four wave-lengths computed from a spectrophotometric comparision of the acetylene and Hefner flames reduced by means of Ångström's curve for the latter.

Gas and Petroleum Flames.

In spite of the fact that the ordinary gas flame is somewhat indefinite, as regards the character of its spectrum, owing to the variations in the character of the fuel consumed and the temperature of combustion with different burners, it is of interest to determine the general character of such flames since these have frequently been employed as sources for spectrophotometric comparisons. Koettgen in the article already referred to has measured the spectrum of ten gas flames with reference to the Hefner lamp. The distribution in the energy of three of these, described as the *Triplex lamp*, *Siemen's precision burner* (*No. 1*) and *Sugg's burner*, have been computed by means of Ångström's curve. The results are given

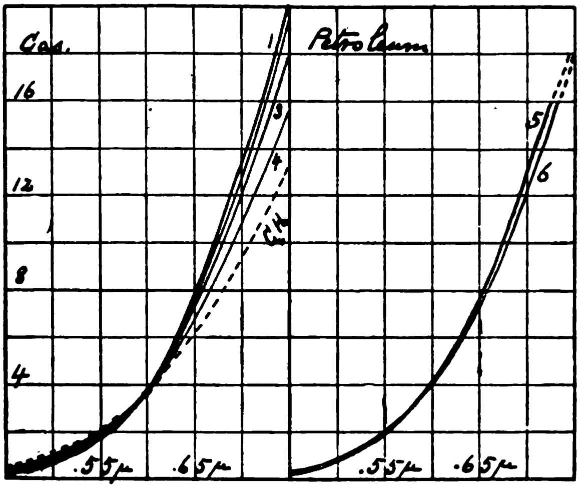

Fig. 2.

in Table II. together with the corresponding data for an ordinary "bats-wing" burner the relation of which to the acetylene spectrum was known. The results are plotted in Fig. 2 in which the corresponding curve for acetylene is shown in broken line for purposes of comparison. The ordinates of these curves are all the same for wave-length .590 μ and are equal to that of Ångström's curve for the Hefner flame. The curve for the triplex burner (1) is almost identical throughout with the curve for the Hefner lamp. The others lie between it and the acetylene curve. These curves, and the same is true of the other curves in the present paper, give the actual distribution of intensities in the visible spectra of the sources to which they pertain and their areas are proportional to the light-giving energy. The question of the energy of visible radiation from the various sources of light to be considered is discussed in a subsequent paragraph.

Table II.

Distribution of Intensities in the Spectra of Ordinary Gas Flames.

Wave-Lengths.	From Comparisons with Hefner Flame (Koettgen's Data).			From Comparison with Acetylene Flame.	
	Triplex Burner.	Siemens No. 1.	Sugg's Burner.	Wave-lengths.	Bat's Wing Burner.
.45 μ	0.19	0.22	0.27	.45 μ	0.11
.49	0.63	0.70	0.81	.50	0.52
.51	.98	1.07	1.17	.55	1.76
.55	1.92	2.00	2.07	.60	4.40
.59	3.50	3.50	3.50	.65	7.70
.61	4.80	4.69	4.63	.70	12.70
.65	8.01	7.34	7.04		
.69	12.48	10.8	10.0		

Koettgen has also compared the flames of seven petroleum lamps with the Hefner flame. One of these, the flame of an ordinary lamp with a flat wick (curve 5, Fig. 2) is of greater importance than the others since it is of a type that has been used in a number of spectrophotometric comparisons. Its spectrum corresponds very closely with the Hefner and with the triplex gas burner. Six of the seven lamps investigated by Koettgen would have intensity curves lying between those of the triplex burner and of the Siemen's precision burner, curve 3, Fig. 2. Only one of the entire set of petroleum flames given in Koettgen's table lies outside these limits and this one, the flame from the lamp known as the *Triumph patent* (curve 6, Fig. 2) differs but slightly from the Siemen's gas burner in its distribution of intensities. Curves 5 and 6 may be taken as representing the extremes of variation in ordinary petroleum flames, the range of which appears to be much smaller than that of gas flames.

TABLE III.

Distributions of intensities in the spectra of petroleum flames, from comparisons with the Hefner flame (Koettgen's data).

Wave-Lengths.	Flat Burner.	Triumph Burner.
.45	0.22	0.23
.49	0.81	
.51	0.99	1.11
.55	1.94	2.03
.59	3.50	
.61	4.76	4.73
.65	7.42	7.36
.69	11.50	11.40

INCANDESCENT CARBON.

The spectrophotometric data available for the computation of energy in the visible spectrum of incandescent carbon is contained chiefly in my articles on the visible radiation from carbon[1] and in Blaker's[2] spectrophotometric comparisons of the light from the filament of incandescent lamps. The former of these investigations consisted in spectrophotometric comparisons of the light from untreated carbon rods at temperatures between 1273° abs. and 1673° abs., with that of an acetylene flame. The relative measurements of different wave-lengths have been reduced to absolute intensities by the use of the curve for the acetylene flame in Fig. 1, and the results are given in Table IV. which shows the distribution of intensities for various parts of the spectrum in the case of a carbon rod heated successively to 1273°, 1373°, 1473°, 1573° and 1673° of the absolute scale.

These values for the three temperatures 1273°, 1573° and 1673° abs., reduced to a common ordinate in the yellow for comparison

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[1] Nichols, PHYSICAL REVIEW, Vol. XIII., p. 65; Proc. of the American Academy of Arts and Sciences, Vol. XXXVII., p. 73.

[2] Blaker, PHYSICAL REVIEW, Vol. XIII., p. 345.

TABLE IV.

Intensity of the spectrum of an untreated carbon rod at various temperatures of the absolute scale.

Wave-Lengths.	Intensities (Absolute).				
	1273°	1373°	1473°	1573°	1673°
.45	0.054	0.121	0.320	0.62	4.32
.50	0.220	0.642	1.93	3.60	19.5
.55	0.815	2.99	7.94	16.51	63.7
.60	2.00	9.01	23.9	55.58	168.7
.65	6.93	28.0	63.0	141.1	315.0
.70	21.2	70.4	162.1	289.5	530.7
.75	52.1	174.0	352.0	578.1	883.6

with other sources, are given in Table V. They correspond, approximately at least, to those which would be found for carbon rods having the temperatures in question but of such a size as to possess in every case the same illuminating power as the Hefner lamp.

TABLE V.

Untreated Carbon.—Continued.

Wave-Lengths.	Intensities (Reduced).		
	1273°.	1573°.	1673°.
.45	—	0.08	0.16
.50	0.20	0.26	0.44
.55	1.20	1.40	1.58
.60	4.21	4.08	4.01
.65	13.9	10.30	7.56
.70	42.5	21.1	12.73
.75	104.0	42.2	21.20

The reduced intensities for these three temperatures are likewise shown graphically in Fig. 3. The unreduced intensities are so great, especially in the red, that they cannot be represented upon the same scale with the other curves in a diagram of reasonable dimensions. The general trend of the curves and their close similarity in character to those obtained with gas and oil flames will be evident from the figure.

Ångström, in the paper already cited, gives a curve for the distribution of intensities in the visible spectrum of an incandescent lamp the filament of which, measured by his method, had a temperature of 2000° abs. This curve reduced to correspond at wave-length .590 μ with the curve for the Hefner flame, is likewise given for the sake of comparison in Fig. 3.

In the course of my investigation of the visible radiation from carbon, just cited, observations were made on carbon rods previously treated by flashing in an atmosphere containing hydrocarbon vapors. The surface of the rods was thus coated with a deposit of the well known silvery gray form of carbon characteristic of the treated filament of the incandescent lamp. Spectrophotometric measurements at temperatures from 1600° abs. upwards, showed the development of an interesting and unexpected deviation from the usual law

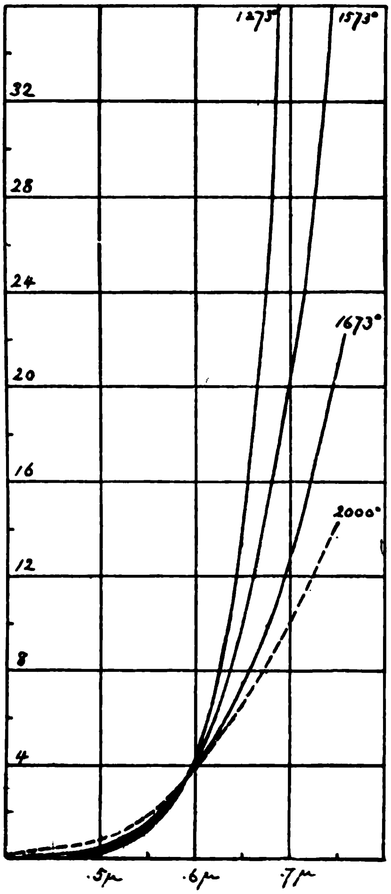

Fig. 3.

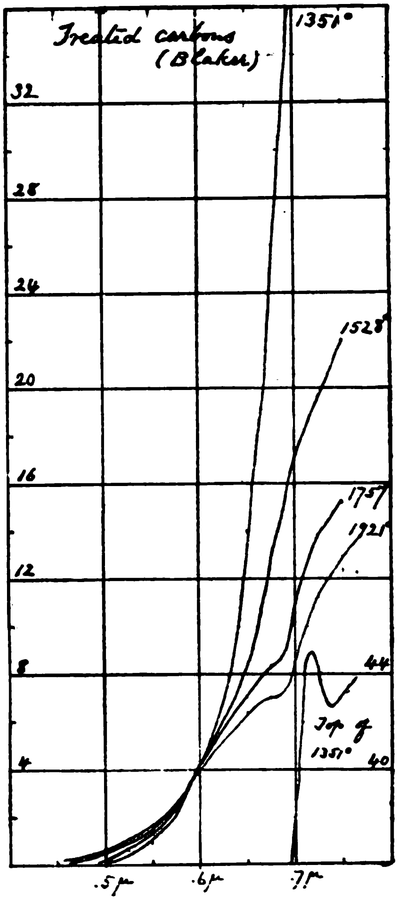

Fig. 4.

of radiation for carbon and this phenomenon was subsequently studied in much greater detail by Blaker.[1] As he likewise used the acetylene flame as a reference source in his measurements it is possible to reduce the spectrophotometric readings to absolute measure by means of the acetylene curve. The results, in form corresponding to that for untreated carbon in Fig. 3, are given graphically in Fig. 4. In these measurements, which were made upon the filament of an incandescent lamp, it was not possible to determine the temperatures directly by means of a thermo-junction as had been done in my investigation of untreated rods. The temperatures given are estimated by means of the relation between the resistance and temperature in such filaments as determined by Le Chatelier.[2] While it is not likely that the scale of temperatures in Blaker's work is directly comparable with those for the untreated carbons, or with the temperature of the incandescent lamp measured by Ångström, it is at least instructive to compare the curves obtained. The curve for Blaker's lamp at 1671° abs. is accordingly plotted

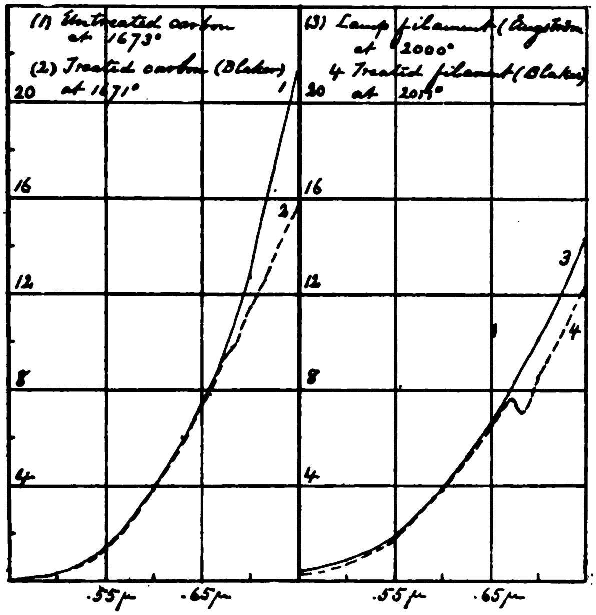

Fig. 5.

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[1] Blaker, *l. c.*

[2] Le Chatelier, Journal de Physique, (3), Vol. I., p. 203.

on the same scale as the curve for the untreated carbon rod at 1673° and the corresponding curve for Blaker's lamp at 2011° abs. with the incandescent lamp measured by Ångström (see Fig. 5). It will be seen that the curves are almost coincident as far as wave-length .65 μ beyond which the intensities for treated carbon fall off and the marked selective radiation of the latter begins to manifest itself.

THE ELECTRIC ARC.

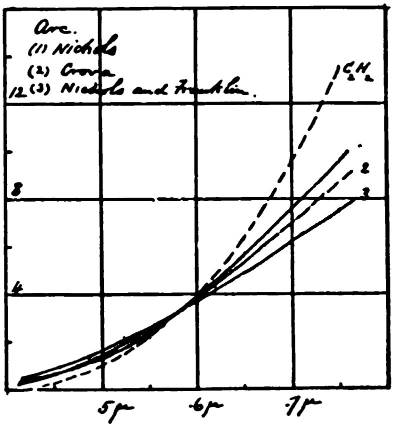

Fig. 6.

Although numerous spectrophotometric studies of the electric arc have been made, but few of these cover a sufficient range of wave-length to be available for the determination of the distribution of intensities throughout the visible spectrum. The three curves in Fig. 6 are from data (Table VI.) computed from measurements by Crova,[1] by W. S. Franklin and the present writer,[2] and from a comparison of the electric arc with the acetylene flame.[3]

These curves show the type of radiation characteristic of incandescent carbon at very high temperatures, but the idiosyncracies

TABLE VI.

Distribution of intensities in the spectrum of the arc light.

Wave-lengths.	Intensities from Comparisons by		
	Crova.	N. & F.	N.
.45	0.90	0.67	0.65
.50	1.35	1.47	1.67
.55	2.38	2.55	2.59
.60	3.96	3.86	3.73
.65	5.66	5.30	4.87
.70	7.65	7.03	6.28
.75	9.60	8.68	7.55

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[1] Crova, Comptes Rendus, 87, page 322.

[2] Nichols and Franklin, American Journal of Science, Vol. 38, p. 100.

[3] Nichols, Journal of Franklin Institute, Nov., 1900.

peculiar to treated carbon do not appear. The curve of distribution for the arc lamp will necessarily vary with the diameter of the carbons, the length of the arc, the current density and the angle which the line of sight makes with the axis of the lamp. The curves here presented refer to measurements taken under conditions such that light from all portions of the incandescent carbon was received upon the slit of the spectroscope. If the light from the crater alone were isolated, and its spectrum explored, a curve of much higher temperature would be obtained and we should expect to find the maximum of intensities lying within the visible spectrum. I am unfortunately not in possession of data for the computation of such a curve.

INCANDESCENT OXIDES.

The sources of light of this class for which we have the necessary data, for the computation of the distribution of energy, are the Welsbach mantel, the zircon light, the magnesium light and the lime light. The results are given in Table VII. and the corresponding curves in Fig. 7.

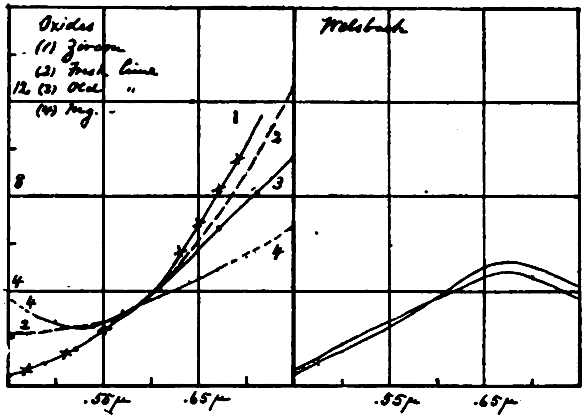

Fig. 7.

It was shown some years ago[1] that the light from the lime cylinder when first heated in the usual way by means of the oxyhydrogen flame differs greatly in character and intensity from that of the same cylinder after prolonged exposure to the action of the flame. These

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[1] Nichols & Franklin, l. c.

TABLE VII.

Distribution of Intensities in the Spectra of Incandescent Oxides.

From Comparison with the Hefner Flame (Koettgen's Data).				From Measurements by Nichols and Franklin.			From Measurements by Rogers.	
Wave-Lengths.	Welsbach (I.).	Welsbach (II.).	Zircon.	Wave-lengths.	New Lime.	Old Lime.	Wave-Lengths.	Magnesium Flame.
.47 μ	0.92	0.72	0.71	.45 μ	2.16	0.42	.45 μ	—
.51	1.91	1.61	1.53	.47	2.16	0.72	.48	2.86
.55	2.71	2.49	2.35	.49	2.25	0.97	.50	2.67
.59	3.50	3.50	3.50	.52	2.53	1.58	.54	2.49
.63	4.33	4.68	5.73	.56	2.73	2.60	.57	3.11
.65	—	—	6.88	.59	3.50	3.50	.61	3.74
.67	4.66	5.19	8.35	.61	4.09	4.09	.64	4.45
.69	4.75	5.04	9.47	.67	7.19	6.77	.67	4.98
.72	4.21	4.72	—	.75	12.6	9.51		

spectrophotometric measurements form the basis of curves 2 and 3 in Fig 7. Curve 2 represents the distribution of intensities of the freshly ignited lime. It differs from the various curves of incandescent carbon in the great excess of energy of shorter wave-lengths. The ordinate at wave-length .45 μ for example is about nine times as great as that of the Hefner flame and about four times as great as that of the arc in the same region. In the course of ten minutes after ignition the brightness of these portions of the spectrum suffers decadence, rapidly at first and then more and more gradually, and the distribution of energy in the spectrum goes over into the form indicated in curve 3. During this interval of time, however, what may be termed the permanent incandescence of the lime increases by the gradual heating up of the cylinder and the curve approaches nearly in form that of incandescent carbon; as may be seen by comparing curve 3 with the curves of the arc lamp. A detailed study of these changes has long since been described.[1] The curve of the Zircon light (1), Fig. 7; deduced from measurements by Koettgen, is identical with that for the old lime through the shorter wave-lengths of the spectrum but shows greater intensities in the red than either of the curves for the lime light.

The curves for the Welsbach or Auer mantels are from spectrophotometric studies made by Koettgen.[2] These mantels had been in uninterrupted incandescence for twenty-four hours, after which time, according to observations of that investigator, they showed no further material change in spectral distribution. While these two mantels differed materially as to the quality of the light emitted, one being relatively stronger throughout the shorter wave-lengths and correspondingly the weaker in the red than the other, the type of the two curves is the same and they are altogether different from the other curves considered in this paper. The maximum intensity for the visible spectrum lies at wave-length .67μ but whether this is the maximum for the entire spectrum or a secondary maximum due to the selective radiation of the material can be determined only by the exploration of the infra-red.

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[1] Nichols & Crehore, PHYSICAL REVIEW, Vol. II., p. 161.

[2] Koettgen, l. c.

The quantitative study of the spectrum of the magnesium light is difficult on account of the fluctuating character of the flame of magnesium even when burned in lamps with automatic feed. Spectrophotometric measurements of this spectrum have however been made by W. H. Pickering[1] and by F. J. Rogers.[1] From their results, which are in good agreement, curve 4 in Fig. 7 has been computed. Magnesium oxide is the only incandescent solid, for which we have any data, the energy in the spectrum of which is *greater in the violet than in the yellow and green.* It would appear from the form of the curve that there is a maximum in the ultra violet; a suspicion confirmed by the fact of the extraordinary actinic activity of this source of light. The type of the curve is similar to that for freshly ignited lime (curve 2), and it seems highly probable that if it were possible to make measurements upon lime at the instant of ignition, the curve would correspond still more closely to that of magnesia. It is possible to secure such measurements only in cases in which, as in the magnesium flame, the light is derived from the oxide at the instant of its formation by the combustion of the metal.

SUNLIGHT AND DAYLIGHT.

Numerous spectrophotometric measurements of direct sunlight of the light reflected from the sky and in various conditions of the atmosphere have been attempted. Of these the measurements of direct sunlight by H. C. Vogel,[1] W. H. Pickering,[2] W. S. Franklin and the present writer,[3] and by Koettgen[4] are in excellent agreement considering the varying atmospheric conditions. The determinations of Koettgen, who compared sunlight with the Hefner standard, have been adopted as the basis of computations for curve 2 in Fig. 8. His measurements extend through a greater range of wave-lengths and the comparisons are made with a source of light about which we have more definite information than is the case with the other available data. Measurements of daylight from cirrus clouds by the same writer have been selected for the same reason and the results of the computation are given in curve 3 of that figure. Curve 1 is from the direct spectrobolometric measurements of the sun's spectrum made by Langley.[5]

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[1] Pickering, Am. Jour. of Science, 37, p. 100.

[2] Rogers, Am. Jour. of Science, Vol. 43, p. 301.

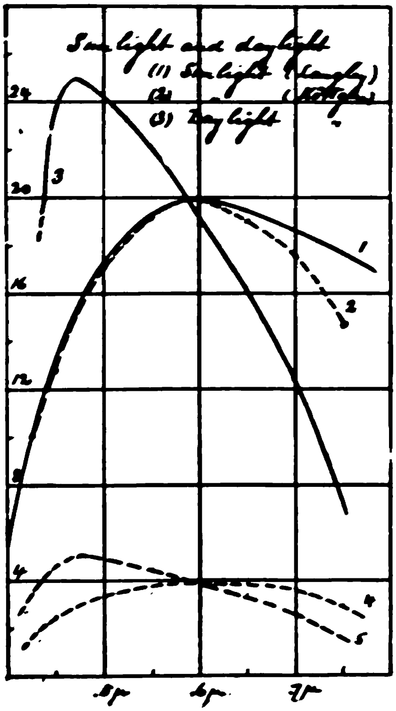

Fig. 8.

These curves are drawn with greatly increased ordinates. Plotted to the same scale as in previous figures curves 2 and 3 would appear as shown by the dotted lines 4 and 5.

It is noteworthy that curves 1 and 2 not only have the same maximum but are closely coincident excepting in the red. The divergence in that region is due to the selection of Langley's smoothed curve which was drawn tangent to the crests of the maxima in that region and so does not show the effect of atmospheric absorption.

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[1] Vogel, Berliner Monatsberichte, 1880, p. 801.

[2] W. H. Pickering, Proc. Am. Acad. of Arts and Sicences, Vol. 15, 1880.

[3] Nichols and Franklin, American Journal of Science, Vol. 38, p. 100.

[4] Koettgen, l. c.

[5] Langley, Researches on Solar Heat, 1884, p. 139.

A COMPARISON OF THE ENERGIES OF VISIBLE RADIATION.

The areas of the various curves of distribution of intensity, already described, taken between the red and violet limits of the spectrum, afford a measure of the total energy of luminous radiation from the sources of light to whose spectrum the curve applies. Ångström's value for the light energy of the Hefner standard flame is

$$20.6 \times 10^{-8} \frac{\text{grm. cal}}{\text{sec. cm.}^2};$$

the square centimeter of surface being situated at a distance of one meter from the flame in a horizontal direction. Reducing this numerical quantity to ergs, a more convenient unit for this purpose, we find that a square centimeter of surface at a distance of one meter from the Hefner flame receives *8.3 ergs per second* of light-giving energy. Assuming that the various curves in this paper

TABLE VIII.

Temperatures and ergs per lux-centimeter-second.

Source.	Ergs.	Temperature.[1]	Source.	Ergs.	Temperature.
Carbon rod (untreated).	29.0	1273° abs. *thj.*	Hefner flame.	8.68	1934° abs. P. 1830° " *A.*
	23.1	1373° "			
	17.8	1473° "	Petroleum flat flame.	8.69	
	14.2	1573° "			
	9.14	1673° "			
Lamp filament Ångström.	7.26	2000° " *A.*	Gas Triplex.	9.13	1897° " P.
			Gas Batswing.	8.40	2053° " *thj.*
			Gas Siemens.	8.26	
			Gas Sugg.	7.70	
Lamp filament (treated). Blaker.	18.5	1351° " *Ch.*			
	9.69	1528° "	Acetylene.	7.12	2173° " *thj.* 2876° " P.
	7.38	1631° "			
	7.34	1769° "	Zicron.	7.17	
	6.35	1921° "	Lime old.	5.89	
	6.42	2011° "	Lime new.	7.21	
Arc Nichols.	5.92		Welsbach. (I.)	4.39	2450° " P.
Arc Crova.	5.85	4025° " P.	Welsbach. (II.)	4.50	2073° " *thj.*
Arc N. & F.	5.79	3690° " W. & B.[2]	Magnesium flame.	5.53	2258° " *thj.*
			Sunlight.	4.85	5068° " P.
			Daylight.	5.53	

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[1] Temperatures marked *thj.* have been determined by the thermojunction; *A.* by Ångström's method; *Ch.* by Le Chatelier's formula; P. by Paschen's equation.

[2] Waidner and Burgess, PHYSICAL REVIEW, Vol. XIX., p. 241.

represent sources all of which are of equal photometric intensity (namely, one Hefner) so that in every case the illumination is one lux, the ergs per second received upon a square centimeter of surface at meters distance from each of the various sources of light in question will be given by multiplying the ratio of the area of the corresponding curves to the area of the curve for the Hefner flame, by 8.63. It has been assumed, as already stated, that curves plotted with equal ordinates for wave-length .59μ correspond to equal photometric intensities of the sources. The areas of the curves thus plotted have been measured with the planimeter, and the results computed as just indicated are given in table VIII.

It will be seen from the table that the energy for unit illumination is by no means constant. In the case of sources of light whose radiation approximates to the law for a black body, that is to say for sources in which the incandescent substance is carbon, the energy per lux-centimeter diminishes with rising temperature; being 29 ergs per second for the carbon rod at 1273° abs., 7.12 ergs at the temperature of the acetylene flame, 5.92 to 5.79 ergs for the arc light and 4.85 ergs for sunlight.

Treated carbon, which has slightly selective radiation, shows decidedly smaller values than untreated carbon or than the carbon particles in flames. The metallic oxides, which are more strongly selective, furnish greater photometric intensity, per erg of luminous energy, than any of the sources in which carbon is the light-giving substance. Of these magnesium oxide, zirconium oxide and calcium oxide show very powerful selective radiation in the blue and violet, a region which is photometrically unimportant on account of the low luminosity of such waves. The selective radiation of the Welsbach mantel lies in a region near the maximum of luminosity and this source of light accordingly gives a larger photometric intensity per erg than any of the sources examined; namely, 4.39 ergs per lux-centimeter. The Welsbach mantel, however, owes its photometric superiority to a deficiency of red rays and to this deficiency the objectionable green color of this source of light is due.

It is noteworthy that of the incandescent bodies whose radiation approximates to the law for black bodies, the sun affords a maximum of photometric intensity per unit of luminous energy and that *the* *maximum of the energy curve* of the sun's spectrum *coincides with the maximum of luminosity for the normal human eye.* Daylight diffusely reflected from the sky, as in curve 3, Fig. 9, has a smaller photometric intensity per erg than direct sunlight.

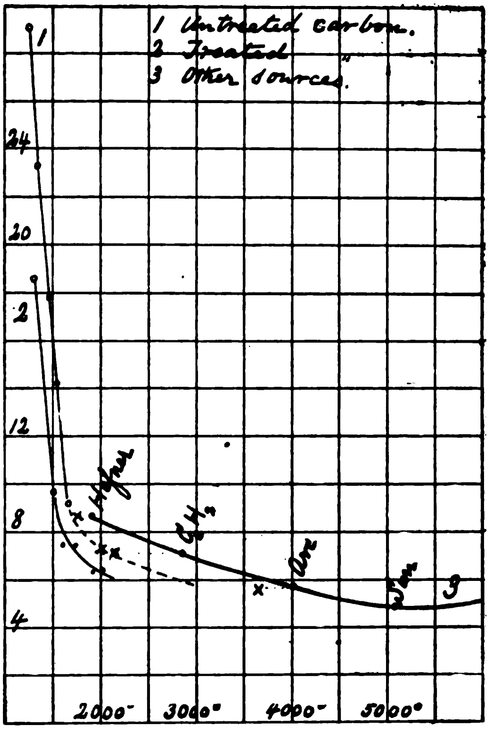

Fig. 9.

RELATIONS BETWEEN TEMPERATURE AND LUMINOUS ENERGY PER LUX-CENTIMETER.

It is obvious that there should exist, at least for sources having a common law of radiation, as in the case of carbon, a definite relation between the luminous energy per lux-centimeter and the temperature of the source of light. Estimates of the temperature of many of the sources already considered have been made by a variety of methods, but unfortunately the results are by no means consistent. If we take those sources for which the maximum of the energy curve has been determined and compute the absolute temperature from

Paschen's equation $\lambda_{max}T = 2,940$, we may plot a curve for which ordinates are ergs per lux-centimeter and abscissæ are temperatures (see curve 3, Fig. 9). Flame sources for which temperatures have been directly determined by means of the thermocouple or by Ångström's method will not fall upon this curve for the reason that absolute temperatures determined by means of Paschen's equation, using Lummer & Pringsheim's constant for a black body, are always much higher for such sources than those obtained by direct measurement. The Welsbach mantel, on account of its peculiar selective radiation falls far below this curve, and the same is true of the flame of the magnesium ribbon as computed from the relative temperature found by Rogers.

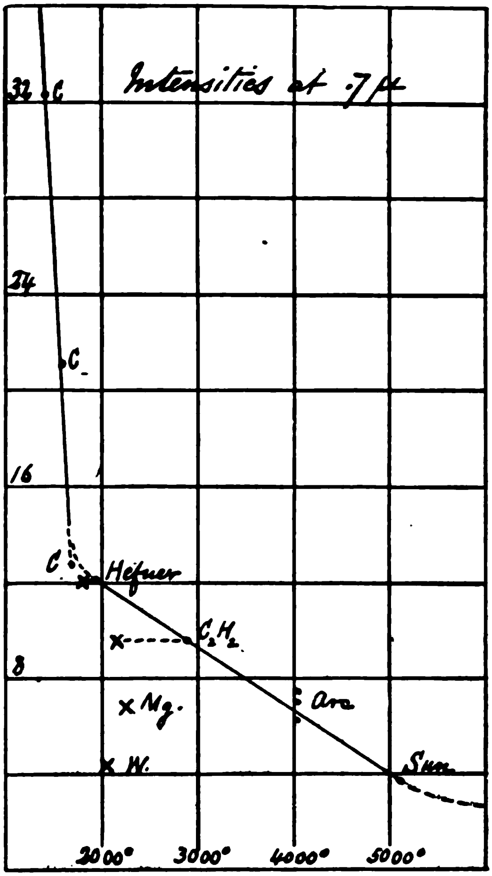

Fig. 10.

In the case of the Hefner lamp, the acetylene flame and the arc, two positions are indicated upon the diagram. The round dots falling upon curve 3 are "λ_{max}" temperatures, the crosses connected with these by a dotted line are respectively the temperature of the Hefner flame as determined by Ångström, that of the acetylene flame from measurements with the thermojunction and the temperature of the arc according to Waidner and Burgess. It seems certain from this figure that if we had consistent measurements of temperature for a body such as carbon between 1200° abs. and the temperature of the arc, the curve would show a sharp inflection at about 1700°. There are definite indications of such a trend in curve 2 for treated carbons and although the measurements with the thermojunction for untreated carbon do not carry us past the point of inflection, the lamp filament measured by Ångström at 2000° abs. lies nearly upon a continuation of curve 1.

If instead of taking the ergs per lux-centimeter we plot the intensity of the spectrum of these sources of light at wave-length .7 μ as a function of the temperature, the ordinates being in each case those which correspond to an illumination of one lux at meters distance, we get the curve shown in Fig. 10, which has an inflection point at the same temperature. Magnesium oxide and the Welsbach mantel, indicated respectively by the crosses "Mg" and "W," lie far below the curve for the carbon sources and it is evident that in optical pyrometry, where the variation of intensity of red light is used in the determination of the temperature of such a source, the "black temperature" will be very much higher than the actual temperature of the glowing body.

Physical Laboratory of Cornell University,
December, 1904.

THE RANGE OF ADJUSTMENT FOR THE CONICAL PENDULUM.

By Frederick Slate.

With the usual arrangement of a conical pendulum, the equation of adjustment for steady motion can be put into the form,

$$\omega^2 \sin\gamma \cos\gamma \,(I_A - A_B) = -\, mgy. \qquad (1)$$

Here γ is the semi-angle of the cone described by the line joining the hinge (H) and the center of mass (C); ω is the constant angular speed about the vertical axis of rotation (HX); I_A and I_B are moments of inertia for the principal axes in the plane of the figure at the point H, HA being often in practice an axis of symmetry. The length HC is r, such that $r^2 = x^2 + y^2$. When adjustment exists, weight and the force distributed from the hinge have for their resultant the system of normal forces, of the type $dN = -\,dmp\omega^2$. And equation (1) expresses directly, for the hinge-axis, the necessary equality of moments between resultant and components, since one component, in this case, can contribute nothing to the moment.

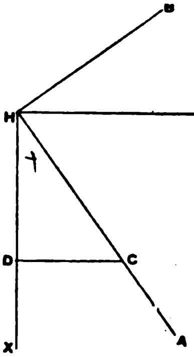

Fig. 1.

Evidently $\sin\gamma = 0$ satisfies the equation for all possible values of ω. Rejecting the factor corresponding to this solution, there remains in general a second solution, given by

$$\cos\gamma = -\frac{mgr}{\omega^2(I_A - I_B)}. \qquad (2)$$

If the ratio in the second member equals unity, the two solutions agree. But so long as $\omega^2(I_A - I_B)$ is numerically greater than mgr there is a second real value of γ. This value is $\pi/2$, if r is zero; otherwise, HC lies above or below HY, according to the relative magnitudes of I_A and I_B. When r is not zero, and $I_A = I_B$, γ becomes imaginary, as an expression of the fact that every line through H in the plane XY is then a principal axis, and all constraining moment is then superfluous at any angle γ. But there is a general failure to recognize and interpret the remaining imaginary values of γ, which present themselves when $\omega^2(I_A - I_B)$ is finite, and numerically less than mgr. There may be an instinctive assumption that γ and ω are in continuous real relation, because $\gamma = 0$, $\omega = 0$ are corresponding values, while other real pairs are observable at finite angular speeds. But this instinct overlooks the truth that $\gamma = 0$, $\omega = 0$ is a pair belonging to the solution $\sin \gamma = 0$. What may interest us, therefore, is to examine *the gap between the solutions*, supposing the inertia constants of the body and the length HC given, the latter different from zero, and ω increasing continuously from zero.

The physical conditions are easily connected with the rectangle (xy), which may be taken, as shown below, to represent, at any position, either the weight moment, or the aggregate moment of the distributed normal forces. In general, of course, the proportional factors for the two force moments thus represented by the same area will be differerent. Adjustment to steady motion, then, corresponds to equality of the proportional factors; and the imaginary values of γ that are here in question will fall within the range where this equality becomes impossible. Let us proceed to determine those factors. For weight moment in any position, the factor (a) is given by the relation

$$axy = -mgy; \quad a = -\frac{mg}{x}. \tag{3}$$

For the normal forces, with the factor (b), the necessary relation is

$$bxy = -my\omega^2 \cdot x_1; \; b = -m\omega^2 \frac{x_1}{x}; \tag{4}$$

since, for the assumed symmetry, the resultant of the normal forces must be a force $my\omega^2$, inward (*i. e.*, parallel to YH), at a distance from H here denoted by x_1. Now, from

$$-my\omega^2 \cdot x_1 = \omega^2 \sin\gamma \cos\gamma \, (I_A - I$$

we obtain, by simple reduction,

$$-\frac{x_1}{x} = \frac{I_A - I_B}{mr^2}; \quad b = \frac{\omega^2}{r^2}(I_A - I_B). \tag{5}$$

Therefore, while the one factor (a) begins at the value mg/r (for $\gamma = 0$), and increases toward infinity as x decreases from r toward zero, the other factor (b) begins at zero ($\omega = 0$), and increases toward infinity with increasing angular speed. No adjustment is possible until the numerical value of the second factor has *overtaken* that of the first. Corresponding to the condition $a = b$, we find

$$\frac{mg}{x} = \frac{\omega^2}{r^2}(I_B - I_A),$$

whence

$$\omega^2 = \frac{mgr}{\cos\gamma\,(I_B - I_A)}. \tag{6}$$

And, for the critical minimum value of the angular speed,

$$\omega\,(\text{min.}) = \pm\sqrt{\frac{mgr}{I_B - I_A}}. \tag{7}$$

For values of ω less than this critical value, we have $b < a$, at the smallest value of a, and the weight moment is in excess of the requisite constraint; *HC* drops back to *HX* from any angle of divergence, however small.

When the rotating body has equal moments of inertia for *CA* and for a parallel to *HB* at *C*, equation (6) assumes the simplified form,

$$\omega^2 = \frac{g}{r\cos\gamma}. \tag{8}$$

In connection with this, it is furthermore easily seen that the impossible values here discussed would necessitate a vertical component of the hinge-force less in magnitude than the weight to be supported; or, otherwise expressed, a perpendicular (*HD*) in the force-triangle (*HDC*), longer than the hypotenuse (*HC*).

UNIVERSITY OF CALIFORNIA.

THE EVOLUTION OF NITROGEN FROM THE CATHODE AND ITS ABSORPTION BY THE ANODE IN GASES.

By Clarence A. Skinner.

RESULTS of experiments have been published recently in the Physical Review,[1] showing the rate of evolution of hydrogen from the various metals when used as cathodes in helium, and also its rate of absorption by the anode when the gas filling is hydrogen. It was found that a fresh cathode gives off hydrogen at the same rate as a water voltameter conceived to be placed in series with the discharge tube, that is the rate of evolution follows Faraday's law for electrolytes. This held with pressures of helium varying from 1 to 3 mm.; with currents varying from 1 to 3 milliampères; and finally with current densities varied from one to six times the *normal* value for the cathode, and with which also was associated a change in cathode fall of about one hundred volts. Then assuming that the evolution in hydrogen was the same as in helium results were given showing that with the hydrogen filling the anode absorbs gas also at a rate following Faraday's law. After the current has passed for a time the rate at both cathode and anode falls below Faraday's law. This is to be expected.

It appeared remarkable that the gas given off by the various cathodes was in all cases hydrogen. Only occasionally was the presence of nitrogen also noted. It is important to know, however, if other gases possess in this respect the same properties as hydrogen. The present paper is a report of the experiments showing that nitrogen plays the same part in carbon electrodes that hydrogen plays in the metals. In addition, observations are given showing that a metal as anode also takes up nitrogen.

First will be given a description of some experiments which led up to the investigation of nitrogen, as the results are of importance in that they reveal the source from which the metals obtain their supply of gas, and further that a metal cannot be freed entirely of absorbed gas by use as cathode.

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[1] Clarence A. Skinner, July, 1905.

The object of these experiments was to obtain a metal free of absorbed gas. Zinc, which has rather a low boiling point, was distilled in glass combustion tubing in an atmosphere maintained by continuous pumping at about .2 mm. pressure. After distillation it was removed, worked into the required form by a clean cutting-tool, then mounted with a similar electrode of ordinary zinc in the electrode tube. This tube was thereupon evacuated and allowed to stand in connection with a drying chamber over night. Tested as cathode the next day in helium the distilled zinc was found to give off hydrogen at the same rate as the one that had not been distilled. It had evidently gained a supply from the necessary exposure to the atmosphere, as it would hardly be expected to hold hydrogen at the temperature and gas pressure at which it had been distilled. Thinking therefore that it must be largely a surface occlusion the electric current was maintained from it as cathode with the hope that soon all gas might be driven off. An interrupted run extending over ten days proved this to be a fruitless undertaking. The evolution of gas decreased to an almost inappreciable quantity, but a spectroscopic observation of the cathode revealed, to the last, hydrogen and nitrogen lines which were clearly marked though less brilliant than those of the helium. The nitrogen radiation was almost wholly absent during the first run of about an hour, but with successive tests gradually grew brighter, remaining finally but little changed in intensity after the hydrogen radiation had diminished perceptibly. The gas filling during these runs was repeatedly purified by a Na,K cathode discharge. This proved after a time ineffective, so the old Na,K discharge tube was replaced by a fresh one. This change necessitated the admission of air for a short time to the electrode tube. Then having been left evacuated over night a test the next day showed that the zinc had regained a new supply of gas which differed in no perceptible way from the first. These experiments prove therefore that a discharge from the metal as cathode will not wholly free it of absorbed gases, and that the metal obtains a supply by exposure to the atmosphere, of which it is very likely that moisture is a necessary part

The persistent presence of nitrogen in the distilled zinc, though the quantity given off was small, suggested the possibility of obtaining quantitative results with this gas if carbon, which absorbs it in large quantities, be used as cathode.

EXPERIMENTS WITH CARBON CATHODES IN HELIUM.

A detailed description of the apparatus used is given in the paper to which reference has already been made. Briefly, it consists of an electrode tube in which can be mounted several electrodes in form of circular disks inlaid in glass. These may be used one after the other without opening to the atmosphere. The gas used as filling is admitted through a stop cock and its pressure measured by a MacLeod gauge.

Three carbon disks (15 mm. in diam.) cut from hard arc-carbon were mounted in the electrode tube and this was evacuated and left over night connected with a drying chamber. The next day the slight amount of gas which had been given off was pumped out and helium admitted to a pressure of about three and a half millimeters. With an aluminium disk serving as anode and one of the carbon disks as cathode, a current of 2 ma. was passed through the helium. A spectroscopic observation of the cathode revealed a gradually brightening nitrogen radiation in addition to that of helium. A trace of hydrogen was also observed. The increase in gas pressure with the time the current had been flowing was noted. The results are represented by curve 1 in Fig. 1. If with a helium filling there is no absorption by the anode the quantity of nitrogen given off under the discharge may be calculated from the pressure increase and the volume occupied by the gas, 465 c.c. For making a comparison the direction of the line *F* represents in the figure the rate of increase in pressure required by Faraday's law.

After the above observations, extending over fifteen minutes, were made, the electrode tube was evacuated and fresh helium admitted. A similar test of the second carbon disk, in helium at 3.1 mm. pressure, gave the results represented by curve 2; while from the third disk (gas pressure 3.2 mm.) curve 3 was obtained.

During the first three minutes these different curves diverge widely but over the rest of their extent all three are very nearly parallel to each other, and also, between three and five minutes, they approach closely to the direction of *F*. Beyond the five-minute point their inclination gradually drops below that of *F*. It is probable that during the first three minutes, owing to the increase in temperature of the cathode surface, uncharged gas is also freed from the cathode, the quantity depending on its concentration in the carbon. The fact that all three curves run parallel to each other beyond this point, and at this point are also parallel to *F*, indicates that the liberated gas carries as negatively charged atoms all of the current between cathode and helium for the first five minutes of discharge.

As observed with metals, carbon also recovers a supply of gas by diffusion from within. Immediately following the series of observations just described the electrode tube was evacuated, then after a six hour's rest, the first carbon tested again. The results were identical with those obtained in the first series from the second carbon. They are represented by crosses on curve 2.

EXPERIMENTS WITH CARBON ELECTRODES IN NITROGEN.

Experiments with metals having shown that in a hydrogen-filling the metal as anode absorbs hydrogen according to Faraday's law, similar experiments with carbon in a nitrogen-filling were performed.

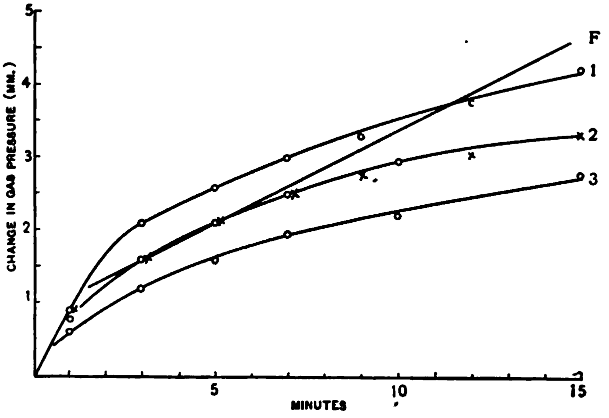

Fig. 1.

Two carbon disks of equal discharge area were used as electrodes and a current of 2 ma. was passed through nitrogen (1.8 mm.).

The change in gas pressure with time of flow for two separate experiments is represented by curves 1 and 2 in Fig. 2. No trace of hydrogen could be detected in either case. The gas pressure rose for a time differently in the two experiments, but reached a maximum value for both at the same time (three minutes). It then decreased at the same rate in both up to the end of the fifteen-minute run. These results appear nearly related to those obtained in helium.

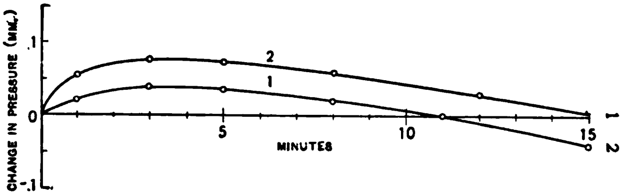

Fig. 2.

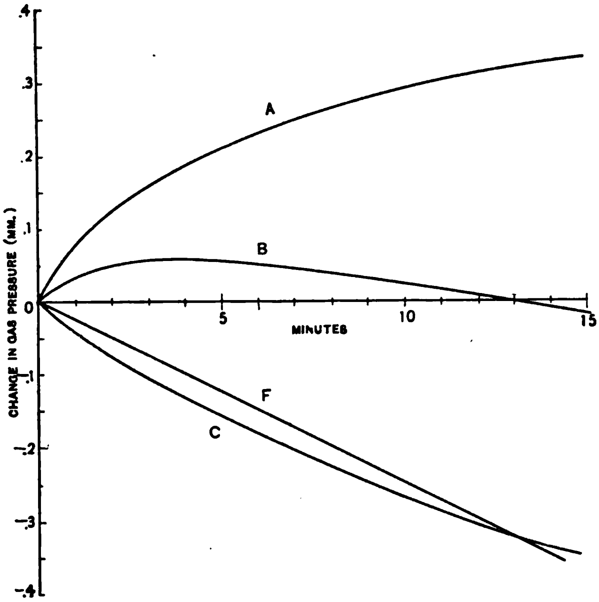

Fig. 3.

Separate experiments give here as there divergent results for the first three minutes but after that time they agree closely.

If now a carbon anode does not absorb helium, and a carbon cathode gives off gas at the same rate in nitrogen as in helium, the effect of the carbon anode in nitrogen is what causes the difference in form between the curves of Fig. 1 and those of Fig. 2. In Fig. 3 curve *A* is the mean of those in Fig. 1, and curve *B* the mean of those in Fig. 2. *B* therefore represents the combined effect of carbon electrodes in nitrogen, while *A* is assumed to represent that of the cathode alone. Now if *A* be subtracted from *B* the resultant curve *C* shows the absorption of gas by the anode. This curve lies unexpectedly close to the direction of the Faraday law line *F* over the whole range. Its absolute value however is too great owing to the wide divergence in results from the separate experiments for the first three minutes of current. The close agreement exhibited by these after that time makes the results however reliable. For seven minutes at least we conclude that the carbon anode takes up all nitrogen atoms discharging to it. The concentration then reaches such a magnitude that uncharged gas is given off by it at a gradually increasing rate.

EXPERIMENT WITH A CARBON CATHODE AND AN ALUMINIUM ANODE IN NITROGEN.

Since nitrogen is contained to only a very slight extent in metals it is of interest to know if they take it up when used as anode in it. An experiment was performed with two points in view. The first was to decrease if possible anode absorption in nitrogen in order to prove that a carbon cathode evolves gas at the same rate in nitrogen as in helium. The second was to test if the metal as anode does take up nitrogen.

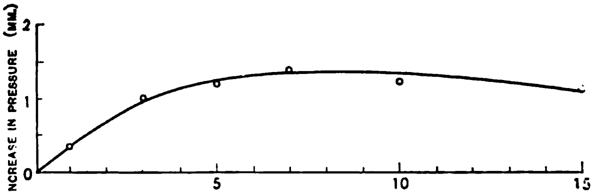

Fig. 4.

With a carbon disk as cathode and an aluminium anode of less than one twentieth its area a current of 2 ma. was passed through nitrogen (1.9 mm.) and pressure measurements made as before.

The results are represented by the curve in Fig. 4. The aluminium surface during this run turned to a dusty brown color as if there were chemical union taking place between metal and gas instead of a physical absorption. The gas pressure increased more rapidly than when either of the carbon anodes were used. A maximum value was reached at seven minutes after starting, instead of three; then a slight decrease in pressure, less rapid than with carbon took place. A comparison of this curve with those of Figs. 1 and 2 indicates that as anode absorption in nitrogen decreases, the pressure curve in nitrogen approaches toward that obtained in helium — this supporting the assumption already made that the amount of gas given off by the cathode is the same in nitrogen as in helium.

General Discussion.

Present Experiments.— The results of these experiments with carbon electrodes in helium and nitrogen support in a very satisfactory manner the conclusions suggested by the experiments with metal electrodes in helium and hydrogen, so more general conclusions may in turn be suggested.

With a gas-filling which is chemically neutral and is not absorbed by the substance composing the electrodes, the electric current between cathode and gas-filling is carried by negatively charged atoms of gas which are already to be found in solution in the cathode. These negative atoms give up their charge to the gas-filling by neutralizing positive ions of the gas-filling. If the cathode possesses a sufficient supply of absorbed gas this neutralization takes place outside the cathode indicated by the fact that the gas pressure increases at a rate demanded by Faraday's law. If, however, the absorbed gas falls below a definite concentration it does not go out of the cathode at a rate sufficient to carry the whole current, but this is probably made up by the positive ions of the gas-filling penetrating the cathode and discharging to the absorbed gas inside, just as in the other case, they discharge to it outside the cathode. If these penetrating ions be chemically and physically neutral they will diffuse back uncharged into the gas-filling. This view explains the fact that evolution of gas from the cathode falls after a time below Faraday's law. If the gas-filling be one which remains in absorption in the cathode the penetrating positive ions may, after discharging to the absorbed gas, play in their turn the part of the absorbed gas in transmitting the current, and results, so far as pressure change is concerned, become more complicated.

At the anode absorbed gases are conceived to play a minor part. Just as it appears impossible for a positively charged gas ion to discharge directly to the cathode, so it is considered impossible for absorbed gas atoms in the anode to carry off from it positive electricity. This could only take place by atoms (or particles) of the anode itself, or at least by some absorbed substance, which in electrical union with the substance composing the anode, is positively charged, while the metal atoms are negatively charged. We conceive therefore that, in the main, the current between anode and gas is carried by negative ions of the gas-filling discharging directly to the anode. If these be atoms of a neutral gas (*e. g.*, helium) they diffuse back without charge into the gas-filling. If they are atoms which form a physical or chemical union with the anode substance they will stick to the anode until such a concentration is reached that they are given off again uncharged. This explains the fact that the anode does not affect the gas pressure when helium is used as a filling, but in hydrogen and nitrogen absorption takes place there at a rate determined by Faraday's law.

The basic principles on which these explanations rest may be summed up as follows:

(*a*) With the existence of chemical affinity or the tendency to form a physical solution, the charging and discharging of a gas atom takes place with one kind of electricity but not with the other (*e. g.*, hydrogen and nitrogen will receive from a metal and give up to it a negative charge, but neither receive nor give to it directly a positive charge).

(*b*) With the absence of both chemical affinity and a tendency to form a physical solution negatively charged gas atoms readily discharge to a metal but those positively charged do not.

(*c*) Without the existence of chemical affinity gas atoms carrying charges of opposite sign transmit a current by mutual discharge, separating thereafter uncharged.

If, therefore, a gas be found which, when absorbed by a conductor, becomes positively charged, the conductor negative, we should expect to find cathode and anode phenomena (including electrode fall) interchanged.

Electrode Fall.— An explanation of the great difference in the fall of potential at cathode and anode may be suggested here. The negative gas ion simply discharges to the anode, either being absorbed by it or falling away uncharged. At the cathode either the negatively charged gas must be driven out of it or the positive ions driven into it (to meet the absorbed negative atoms) at a rate sufficient to carry the current. In addition, therefore, to the energy-change by simple absorption or combination at the anode there is at the cathode that absorbed in forcing the charged gas atoms to diffuse through the metal. This appears to be caused by the positive gas ions, under the electric forces bombarding the cathode surface and thereby maintaining a molecular agitation equivalent to that produced by heat. The cathode fall should therefore increase: (*a*) with the resistance to diffusion through the cathode; (*b*) with depletion of absorbed gas in the cathode; (*c*) with the energy required to maintain the dissociation of the gas-filling so that bombarding atoms be furnished. (This latter would therefore increase with the rate of recombination of the dissociated gas.) The energy of absorption of gas by the cathode would also play a part so long as its concentration in the cathode is changing.

The anode fall in nitrogen has been found to increase with use. Copper is a marked example.[1] This probably arises from the increase in concentration of absorbed gas, for use as cathode has been observed to cause the anode fall to return to its original value. Further, Warburg[2] found that if a steel cathode possesses an oxidized surface the cathode fall is thereby greatly reduced so long as the oxide remains. In such a case the current is probably carried by negatively charged oxygen emanating from the surface instead of by gas atoms diffusing out of (or into) the body of the metal. The resistance to diffusion would thereby be greatly decreased. If however the heat of combination of oxygen with steel be greater than that of absorption of hydrogen this latter would tend to neutralize the effect of decreased resistance to diffusion. It is likely, from comparison with the anode fall, that resistance to diffusion in the metal plays generally a much greater part in determining the cathode fall than does energy of absorption (or combination).

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[1] C. A. Skinner, Wied. Ann., 68, p. 752.

[2] E. Warburg, Wied. Ann., 31, p. 545.

This view of the cause of the electrode fall requires that the cathode fall should disappear when the cathode is raised to a temperature that will drive the absorbed gas out of the cathode at a rate sufficient to carry the current. Cunningham has shown that the cathode fall of carbon in rarefied gases decreases as its temperature rises.[1] Wilson[2] has found that hot platinum fails to give of negative electricity when freed of absorbed hydrogen. It is probable therefore that the negative leak from incandescent carbon would disappear if the carbon were completely freed from absorbed gases. Conduction in flames is also greatly facilitated by heating the cathode. Stark and Cassuto have shown that in order to maintain an electric arc the cathode must be at a high temperature while the temperature of the anode is of no effect.[3] It is also known that in the ordinary arc the cathode fall is very small while the anode fall is of the same magnitude as with the glow discharge through rarefied gases. While however the principles enunciated above will apply to the electric arc it is probable that much of the current between the electrodes is carried by the substance composing them. Stark concludes from experiments on the mercury arc that the mercury vapor emanating from both electrodes carries the current — that from the anode carrying positive, that from the cathode negative electricity.

Photoelectric Currents. — The same reasoning followed above in regard to the effect of cathode temperature applies to the effects of light and other radiations on conduction through gases when these radiations fall on the electrodes. The absorbed gas may be freed from both electrodes but only that leaving the cathode can act as carrier of the current. The gas absorbed in the anode cannot receive from it a positive charge therefore must leave either charged negatively or uncharged, but since the anode is positively charged the negative ions of the gas would be held by it and hence only uncharged atoms escape. On the other hand at the cathode the negative ions after being freed would be driven forth by the electric forces. We have thus the radiation affecting conduction when it falls upon the cathode but not upon the anode.

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[1] J. A. Cunningham, Phil. Mag., February, 1905.

[2] H. A. Wilson, Phil. Trans., 202, p. 243, 1903.

[3] N. Cimento, June, 1904.

Conduction of Gases in Vicinity of Metals— It is possible that this may arise at least in part from absorbed gas atoms emanating from the metal. It is known that a sodium-potassium alloy discharges conductors placed in its neighborhood. Now the writer has observed that even after distillation in vacuo pure hydrogen is continuously given off by this alloy. A series of observations extending over more than ten days, with two different samples of it, showed that from about seven square centimeters of surface .1 to .2 c.c. of hydrogen (at atmospheric pressure) is liberated per day when the gas pressure is kept very low. There seemed to be no reduction in quantity liberated as time passed but a variation in daily temperature appeared to cause a change in the quantity given off. Neither sample had a clean metallic surface; both had become tarnished by oxygen and nitrogen.

Contact Potential. — The writer has recently published[1] experimental results showing that a close relationship exists between the series of metals arranged according to the magnitude of their electrode fall in gases and the contact potential series. This is especially marked in case of the cathode fall in hydrogen. The two series are practically identical. It is therefore probable that an explanation of the one will also furnish the principles upon which the other is explicable.

We have concluded that in gases positively charged ions will not discharge directly to a conductor while the negative ions give up their charge readily and with it are generally absorbed. If therefore two metals be placed in an ionized gas together, the positive ions will remain in the gas while the negative are absorbed at a certain rate by the metals. The metal which absorbs these most rapidly becomes negatively charged with respect to the other. This difference in charge increases until the difference of potential between them produces a sufficient electromotive force to cause absorption in both to take place at the same rate. After that there is no further change in potential difference of the two metals. For example, aluminium which becomes, in contact with platinum, negatively charged, is supposed to absorb the negative ions in the gas-filling more rapidly than platinum. This agrees with the results in rarefied gases; for, tested as cathode in gases aluminium is found to give up hydrogen more freely than platinum does and also as a consequence of this possesses a lower cathode fall.

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[1] Phil. Mag., September, 1904.

Physical Laboratory, University of Nebraska, Lincoln.

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THE RESIDUAL ELECTROMOTIVE FORCE OF THE CARBON ARC.[1]

By G. G. Becknell.

In the course of some recent experiments on unipolar conductivity between metallic plates, it was suggested to me by Professor Crew that I examine the somewhat similar case afforded by the intensely heated region between the electrodes of a carbon arc *immediately after its interruption.*

The circuit was so arranged that the dynamo and galvanometer could, by means of a double-pole double-throw switch, be alternately joined in series with the arc-gap. (See Fig. 1.)

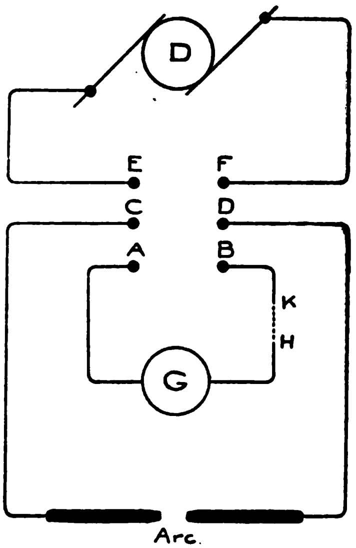

Fig. 1.

It was found at once that a current, which we may call the *residual current,* could be observed for more than ten seconds after the interruption of the arc; and it was seen, upon replacing the galvanometer by a Weston voltmeter, that the residual electromotive force was counter to that of the dynamo, and reached a maximum value of more than half a volt.

In order to show something of the qualitative nature of the phenomenon, the following simple experiments were tried:

1. A plate of either copper or mica, *i. e.,* a plate of material either conducting or non-conducting, when interposed between the electrodes without touching either of them, was sufficient to arrest the residual current entirely; but upon the removal of the plate the current was immediately reëstablished.

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[1] A paper read before the American Physical Society, April 21, 1905.

This experiment with the copper plate shows that the residual effect can hardly be due to thermo-electric contact (whatever that may mean) between the heated carbon tips and the heated gases of the arc, for in such a case the interposition of a copper plate across the arc-gap would tend to increase the current through the galvanometer, and certainly not to destroy it.

2. A short copper wire joining the positive and negative electrode was sufficient to stop entirely the residual current *through the galvanometer*, showing that the effect cannot be traced to a thermoelectric source existing *outside* the arc, for in this event the current would have been much increased by thus cutting out the resistance of the arc-gap. We may fairly conclude then, perhaps, that the residual current is due neither to a thermoelectric effect in the arc nor to one external to it.

3. As a further test a gentle air-blast was applied to the region between the carbons at the instant when the galvanometer was thrown into the circuit. This again had the effect of removing nearly all traces of the residual current as long as the air current was continued, unless the poles were placed as nearly together as one millimeter, and even then the effect was reduced to one tenth. The failure at this point to completely destroy the effect was probably due to the partial inaccessibility of this small region to the current of air. It was found also that when the air-blast was discontinued the residual current was set up again, provided the blast had not been applied for a time longer than four or five seconds.

4. It was observed also that if the galvanometer was thrown off and the dynamo thrown on to the arc-gap for a few seconds, thus producing an electric field, *but no arc*, between the electrodes, a smaller residual current was reëstablished in the same direction as before, that is, counter to that of the dynamo. This effect could be detected if tried within a minute or two after the interruption of the arc.

It would seem from these experiments—the interposition of the mica sheet, and of the readily conducting copper, as well as the effects of the air-blast, and the renewal of the electric field, that we have here not a case of ordinary electric *conduction*, but probably one of electric *convection.* This view is strengthened by the fact that the *alternating* arc gives a very small residual effect.

In attributing this current to convection it is not meant to imply that this is an explanation of the phenomenon. On the contrary the ionic explanation of it, which I shall offer at the close of this article is not entirely satisfactory, or at least is not complete.

Now passing to the quantitative side of this phenomenon, I proceeded as follows to measure the residual electromotive force and current as functions of the time.

A rotating switch of special design was employed to automatically break the dynamo circuit at any desired instant, then after a definite and measurable interval which might be varied at will, to throw the galvanometer into circuit with the cooling arc-gap for a definite fixed period which also might be varied if desired.

This rotating switch consists essentially of two similar vulcanite discs fitting face to face, each graduated in degrees, and capable of being set in any desired phase with relation to one another. Both are clamped to a shaft by means of a lock-nut, and the device is kept in uniform rotation with a period of ten seconds by means of a constant-speed motor. On the outer face of each of the disks is inlaid a silver strip of particular design, each strip passing under its own metallic brush.

One of these strips, coming into contact with its corresponding brush closes the circuit of an electro-magnet which acts upon a wooden rocker-arm, and thus through mercury cups connects the arc with the dynamo for a definite interval.

As soon as the first silver strip passes off its brush the circuit of the electro-magnet is broken, the rocker-arm is released and drawn away by a spring cutting out the dynamo circuit at *EC* and *FD*, in Fig. 1, and closing the mercury cups *AC* and *BD;* so that as soon as the second strip passes under its corresponding brush, the galvanometer circuit is closed at *GK* at the proper time and during the proper interval.

At the very outset it was observed that the length of time the arc is allowed to burn before measuring the residual electromotive force is a very important factor. A steady state seemed to be reached in about one minute, and all my observations have been made after waiting this length of time.

The arc was used in the vertical position, in which it was found to behave in a much more uniform manner than in the horizontal position.

It was found, furthermore, that the magnitude of the residual current is somewhat dependent upon the quality of carbons used. For example, graphite terminals were observed to produce a very small residual effect; however this may have been due to the unsteadiness of the arc.

If results are to be uniform, and the effect to be as great as possible, it is absolutely necessary that the arc be centered, and that it should not be running about the electrodes.

Filing the carbons to a definite shape adds further to the constancy of results, for in this case the arc potential difference, arc current, and pole distance can all be held constant throughout the experiment.

In order to determine the residual electromotive force and current as functions of the time, null methods were employed. The measurement of the electromotive force was effected by means of a Wolff potentiometer, thus balancing the average value of the varying electromotive force during one tenth of a second, against another constant and known electromotive force applied for the same length of time.

In a similar way the varying current was balanced against a known constant current, by the use of a differential galvanometer.

The curves shown in Figs. 2 and 3 were thus determined, cored carbons having a diameter of 1.6 cm. being employed. These carbons were purchased from the Western Electric Co. of Chicago. The impressed electromotive force was 110 volts, the potential difference of the arc 35 volts, the arc current 16 amperes, and the pole distance 4 mm. Both curves rise rapidly within the first quarter of a second, the electromotive force reaching a value of nearly 0.65 volt, and the current a value of 0.55 mil-ampère through a circuit containing 1,000 ohms in addition to the arc resistance. The descent of the current is much more precipitate than that of the electromotive force, showing that the resistance of the arc increases very rapidly.

A very interesting thing is noticed in the behavior of the differential galvanometer when a point upon the rising portion of the curve is being studied. In this case the instrument first gives a twitch in favor of the battery, then immediately after one in the direction due to the arc, thus indicating a rapid rise at the point under consideration. On the falling side of the curve the deflections occur in the reverse order.

The interesting study of the counter electromotive force of the arc which has already been presented to the American Physical Society by Mr. Hotchkiss,[1] as well as that of Blondel,[2] is confined entirely to what happens during the first hundredth of a second after the interruption of the arc. If there have been any other measurements of the quantities here presented, I should be glad to get a reference to them.

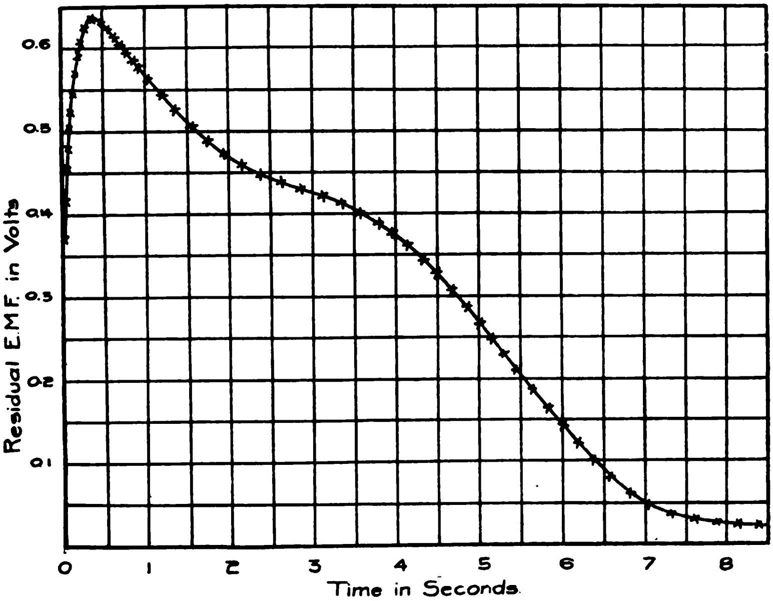

Fig. 2.

Thus far nothing has been said concerning the resistance of the cooling arc; but if the relation between the residual electromotive force, current, and resistance should be that expressed in Ohm's law, it would be an easy matter to construct a resistance — time curve in which the ordinates would be the ratios of the corresponding ordinates of the electromotive force and current curves (Figs. 2 and 3). When such a curve is constructed it is found that the resistance at the end of the first hundredth of a second after the break is about 800 ohms, then gradually increases reaching a value of 1,000 ohms in less than 0.2 of a second.

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[1] Hotchkiss, Bull. Amer. Phys. Soc., Vol. 2, No. 2, 1901.

[2] Blondel, London Electrician, Vol. 39, p. 615; Comptes rendus, Vol. 125, p. 164.

After this the curve rises rapidly, becoming asymptotic to a line parallel to the axis of ordinates. However, upon examining the first part of this curve, remembering that the current was measured with a resistance of 1,000 ohms in the circuit in addition to the resistance of the arc, we find that the resistance of the arc *itself* during the first tenth of a second would be *negative* upon the assumption that Ohm's law expresses the relation between these quantities. We are thus forced to the conclusion that Ohm's law does not hold for the residual current.

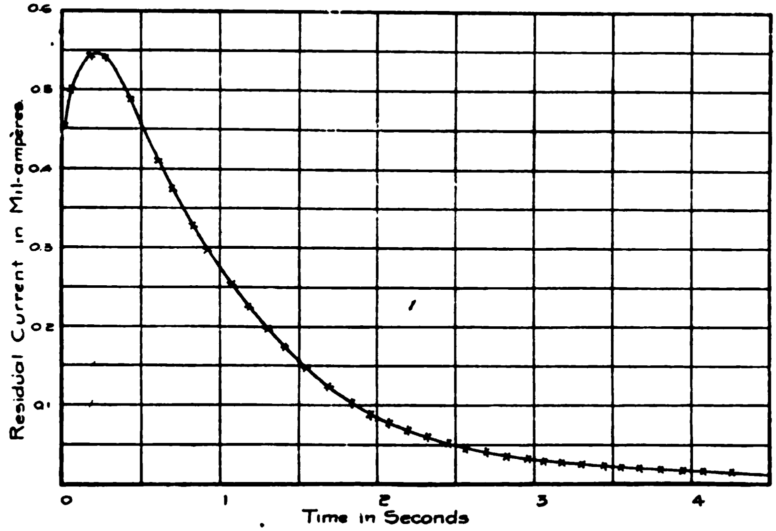

Fig. 3.

NOTE ADDED APRIL 25.

It is possible that an explanation of this phenomenon, in terms of the ionic hypothesis, may be built upon the following facts: first, the carbons of the electric arc are incandescent, and the temperature of the positive terminal is nearly 1000° C. higher than that of the negative terminal; secondly, incandescent carbon is especially efficient in the emission of negative corpuscles, as illustrated in the well-known Edison effect, the rate of production increasing with the degree of incandescence. Then as long as the arc is in operation, the negative ions (emitted in far greater numbers from the incandescent tip of the positive carbon then from that of the negative carbon) are borne not across the arc-gap, but against the electric field back into the positive terminal from which they proceeded. But when the arc is interrupted the conditions are changed. There is no longer an impressed electric field to hold back the stream of corpuscles. They are freely emitted from both incandescent terminals (yet more abundantly from the positive) and diffuse across the arc-gap, this state of affairs continuing until the carbons have so far cooled down that the rate of production of the negative ions by the positive carbon is no longer in excess of the rate of their production by the negative carbon. (See Fig. 4.)

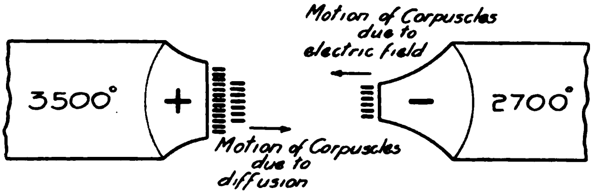
Motion of Corpuscles due to electric field
3500°
+
−
2700°
Motion of Corpuscles due to diffusion

Fig. 4.

With this understanding of the matter it is easy to see why the arc requires a considerable time to reach a state of equilibrium; for this steady state would depend upon a constant difference of temperature between the electrodes, and this could only exist when each terminal had reached its maximum temperature and was so maintained.

The fact that graphite terminals give a small residual effect may be due to the fact that graphite is a fairly good conductor of heat (as ordinary carbon is not) and would thus tend to equalize the temperatures of the electrodes much more readily than ordinary carbons.

As to the maximum which occurs in the curves of both the electromotive force and current (Figs. 2 and 3), it possibly may be due to the very appreciable time required for these ions to traverse the arc-gap; and if this is the case, the time at which the maximum occurs after the interruption of the arc may prove a useful factor in the determination of the ionic velocities.

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SOME PHYSICAL PROPERTIES OF CURRENT–BEARING MATTER. — III. BOILING POINT.

By Paul R. Heyl.

THIS article contains a description of some experiments on the effect of a current on the boiling point of mercury and of two electrolytes, copper sulphate solution and dilute acetic acid. The results are all negative. The boiling point of mercury is not altered by 0.04° by a current density of over 100 amperes per square centimeter, and the electrolytes showed no change as great as 0.001° for current densities of 0.05 with the copper sulphate and 0.001 with the acetic acid.

Mercury.

The general plan of the experiments on mercury was to boil the substance in two vessels, in one of which a current could be turned on at will, and to measure the difference of temperatures by a differential thermocouple. To form the latter a piece of platinum wire about thirty centimeters long was soldered at its ends, by means of zinc, to long pieces of copper wire. Zinc was chosen as the solder because its melting point is above the boiling point of mercury. The two junctions were protected by pieces of drawn out glass tubing and immersed in the vessels of boiling mercury, while the ends of the copper wires were connected to a galvanometer with a key in the circuit. The thermoelectric power of a copper-platinum junction at the temperature of boiling mercury is about ten microvolts per degree, according to Tait's diagram, and the galvanometer (of the Rowland wall pattern) gave a deflection of half a scale division per microvolt, consequently each scale division represented a difference of temperature of one fifth of a degree.

The only difficulty in the carrying out of this plan was to bring about the introduction of a rather heavy current into the boiling mercury without the formation of an arc. This was finally done by introducing the current into portions of the mercury which never rose to the boiling point. Fig. 1 shows the arrangement of the apparatus. A glass *T*-tube about one centimeter in diameter had one arm drawn out and connected by rubber tubing to a small glass funnel. The horizontal arm of the *T*-tube was closed by a small cork through which passed an iron wire *C* and a small glass tube *D*. Mercury was poured into the funnel until it half filled the horizontal arm and an iron wire *B* was inserted into the mercury in the funnel. By the wires *B* and *C* connections were made through a switch, a rheostat and an ammeter to a dynamo. In the vertical arm of the *T*-tube was placed one of the copper-platinum junctions in its protecting tube, the end reaching down into the narrow part *A*. The joint at *E* was open. The mercury was boiled at *A* by applying a very small Bunsen flame, the vapor of mercury being drawn off through the tube *D* by an aspirator, air entering freely at *E* to prevent reduction of pressure. In addition, the tube *D* was made to fit loosely in its cork that air might enter there also if necessary. The cross section of the mercury at *A* was about 0.1 square centimeter, which of course was somewhat reduced by bubbles on boiling. The current was 10 amperes, making a current density of over 100 amperes per square centimeter at the point where the boiling took place. Higher than this one could not go without danger of forming an arc at *A*.

The second copper-platinum junction dipped into boiling mercury in a vessel which presented no features of interest. As in Fig. 1 mercury vapor was removed by an aspirator and a constant level was maintained by a funnel-shaped reservoir.

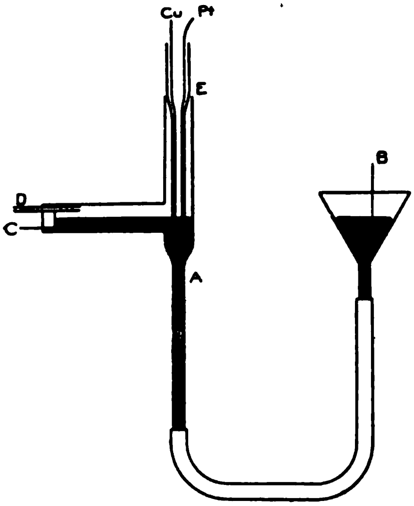

Fig. 1.

The mercury in both vessels being brought to boiling (with no current flowing) the galvanometer circuit was closed. It proved impossible to keep the instrument at zero, the reading varying slowly and irregularly several scale divisions on either side of the zero point. However, there were times when the reading remained stationary at or very near the zero point for several seconds, and by taking advantage of these periods it was possible to make a number of conclusive tests, throwing the current on, maintaining it for several seconds, and interrupting it without altering the reading. A change of one fifth of a scale division would have been easy to recognize, and this would have meant a change in the boiling point of 0.04°.

Electrolytes.

On account of the relatively high resistance of electrolytes one must be content with lower values of the current density and make up for this by more delicate measurements of change of temperature.

The first solution used was copper sulphate, of density 1.12. It is impossible to boil this in glass without some slight bumping, but in copper vessels it boils freely and steadily, and the boiling point may be taken by a Beckmann thermometer to 0.001°.

The first plan was to use a copper beaker as one electrode, dipping another electrode of copper rod into the center of the solution. The thermometer was dipped into the solution half way between the central electrode and the wall of the beaker. On applying to the boiling liquid a current whose average density was one fifth of an ampere per square centimeter there was a decided change in the reading of the thermometer which seemed to depend on the direction of the current. When the current was passed so that copper (and hydrogen) appeared at the inner surface of the beaker the thermometer rose at once, sometimes by as much as two or three tenths of a degree. With the current reversed the effect was usually a much smaller rise, sometimes preceded and sometimes followed by a slight fall. Bearing in mind the effect produced on the boiling point of a liquid by the nature of the surface of the containing vessel it seemed possible that the rapid deposition or removal of copper at the surface from which the steam bubbles took their rise might have been causing the irregular effect noticed. This suspicion was intensified when the thermometer showed no change as great as 0.001° on applying an alternating current of a frequency of 1,800 per minute and a density of 0.07 to the boiling solution.

Five different forms of apparatus were devised in the hope of eliminating the supposed effect of the changing surface before it was discovered that the trouble was due to something entirely different, namely the torrent of gas bubbles that arose from the electrodes. The electrodes, surrounded by a sheath of gas, were undoubtedly warmer than the solution, as in the water pail electric forge, and the bubbles, coming off in torrents, did not cool off completely before striking the bulb of the thermometer.

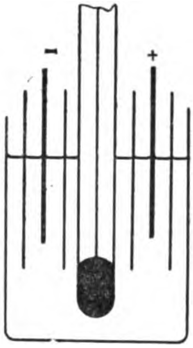

Fig. 2.

In Fig. 2 is shown a form of apparatus which can be used both to demonstrate the source of trouble and to eliminate its effects. The containing vessel is of copper varnished within with shellac. The Beckmann thermometer dips into the center of the liquid, and the current enters and leaves by two heavy copper rods, surrounded by wide glass tubes open at both ends. To reënforce the insulation of the copper beaker its walls were protected by sheets of mica, held in place between the walls of the beaker and the wide glass tubes. All the gas generated passes up the glass chimneys without striking the thermometer, and it is possible to throw on and off the current in the boiling liquid without altering the reading of the thermometer by 0.001°. Of course there were times when the reading fluctuated slightly when there was no current flowing, and the boiling point rose very slowly in the long run on account of the increasing concentration of the solution. As in the experiments with mercury, advantage had to be taken of those times when the thermometer was quiescent.

To test still further the correctness of this diagnosis of the trouble a thermometer was inserted in one of the wide glass tubes. On applying a current to the boiling liquid this thermometer rose promptly about three quarters of a degree and fell again when the current was stopped, while the Beckmann thermometer outside was unaffected. In addition the wide glass tubes were removed and the Beckmann thermometer raised to the level of the electrodes. On turning on the current the thermometer rose at once.

The current density employed in these experiments was about 0.05 ampere per square centimeter in the neighborhood of the thermometer bulb.

Experiments were also made on a five per cent. solution of acetic acid, using carbon electrodes with a form of apparatus otherwise the same as that shown in Fig. 2. On account of the high resistance of this solution the greatest current density that could be attained was 0.001 ampere per square centimeter, and no change as great as 0.001° could be detected in the boiling point.

ON THE VARIATION OF A CAPACITY WITH TEMPERATURE.

By Earle M. Terry.

THE measurements of small changes of capacity due to changes of temperature has been made possible by the use of the alternating current galvanometer. The following is a brief description of a modification of the instrument first used by Stroud and Oates.[1]

It is essentially of the D'Arsonval type, except that the field is built up of laminations of soft iron, and wound so as to be used directly on the 110-volt, 60-cycle, A. C. circuit. In the particular instrument used the laminations are circular disks about 30 cm. in diameter, and built up so as to have a cross-section about 4 cm. square. An opening about 1.5 cm. wide was made to admit the coil, the pale faces being tapered down to about 1 cm. in width.

The coil is made of no. 40 double insulated wire wound on a wooden form, and has a resistance of approximately 350 ohms, and coefficient of self-induction of 50 millihenries.

The great difficulty in manipulating the instrument is due to the fact that a closed coil suspended in an alternating magnetic field takes up a position of great stability, such that its axis is at right angles to the field, or so that the coil itself will include a minimum number of lines of force.

Since in any use of the instrument the coil must necessarily be closed through a greater or a less resistance, this stability reduces the sensibility enormously. Stroud and Oates overcame this difficulty by winding the coil upon a broad copper frame, in which the foucault currents induced in the sides acted like a closed coil placed at right angles to the galvanometer coil. This effect was made to predominate so that the coil, when on open circuit, took up a position so as to include a maximum number of lines of force, and was then brought back to zero by shunting with a suitable resistance.

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[1] Phil. Mag., Dec., 1903.

The chief objection to this method of control is that it necessarily limits the range for which the instrument is sensitive. For if the external circuit includes capacity, the leading current produced by this in the coil will have the same effect as the torque on the sides of the frame, necessitating so small a shunt resistance as to greatly reduce the sensibility, as well as cause an annoying drift in the zero.

This action can probably be best explained by reference to a vector diagram, Fig. 1.

If *OA* represents the flux in the field, then the vector *OB* would represent the current induced by it in the galvanometer coil, providing it had no inductance, but simply resistance. There would then be no force acting upon the coil, for the product of two vectors at right angles is zero. Since, however, the coil possesses inductance, the current lags behind *OB* and may be represented by a vector such as *OC*. The component *OD* of this vector being 180° behind *OA* gives the repulsion producing the objectionable stability.

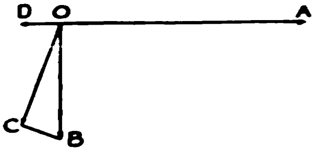

Fig. 1.

If a capacity be placed across the coil sufficient to swing *OC* ahead until it has the direction *OB*, then the conditions of maximum sensibility is reached. If, however, the capacity be still further increased, so that the current has a component in the direction *OA*, then there will be an attraction and the coil will swing around so as to include a maximum number of lines of force.

The author has made use of this fact as a method of control and the manipulation of the instrument then becomes very simple. It is connected up the same as an ordinary galvanometer, except that no key should be placed in the galvanometer circuit, as the position of the coil depends upon the external circuit. If the set up contains both inductance and capacity, these will serve as part of the control, it being only necessary to shunt across the galvanometer coil with sufficient conductivity or capacity, as the case may be, to bring the galvanometer to a suitable zero point and sensibility.

One of the first uses to which the instrument was put in the laboratory at Madison was the measurement of an inductance by

Anderson's modification of Maxwell's method. Since the set up here contains both inductance and capacity, it was found that the capacity could be adjusted so as to make the galvanometer sufficiently sensitive and no control whatever was needed.

As it was necessary to first obtain a steady current balance, a double throw switch was placed in both the galvanometer field and the battery circuits, so that when rocked one way the instrument could be used to obtain the direct current balance, and when rocked the other way, to obtain the balance for the variable state.

In a set of five determinations made in this way, keeping the capacity constant and varying the resistances, the outstanding difference was 2 parts in 20,000 or .01 per cent. The precision of setting, however, was much closer than this, but the resistances could not be depended upon to a closer degree of accuracy.

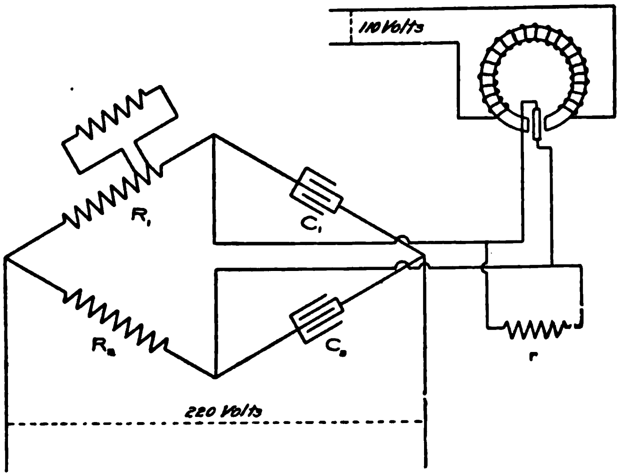

Fig. 2.

It was found that no such agreement in results could be obtained on different days, which lead to the suspicion that the capacity must have an appreciable temperature coefficient.

In order to determine this, the bridge method for comparing capacities was used. The apparatus was arranged as shown in Fig. 2. The two capacities were subdivided condensers manufactured by Elliott Bros., having a range from .05 to 1 microfarad. The one labelled C_1 was but recently purchased and was used as the standard, while C_2 has been in use for several years, and is the one for which the temperature coefficient was determined.

Both capacities were placed in tin boxes immersed in large water baths. C_1 was held at a constant temperature, while C_2 was varied between 17° C. and 33° C. The water in tank no. 2 was kept constantly stirred by two turbines driven by a water motor, while the temperature could be held at any point by means of a thermostat to .1° C. for any desired length of time. Owing to the large thermal capacity of the condenser it usually took about 48 hours for it to come to a uniform temperature throughout. This condition could of course be detected from the constancy of the capacity.

The resistances were new boxes manufactured by Otto Wolff, and could be relied upon to .01 per cent. In order to obtain a sufficiently fine adjustment a small portion of one of the boxes was shunted by a variable resistance, always large.

All connections were made of no. 12 heavily insulated copper wire.

An alternating pressure of 220 volts was applied to the bridge, while the galvanometer field was excited by 110 volts from half the secondary of the same transformer. Inasmuch as the capacity across the galvonometer coil was comparatively large the conductivity in the bridge being always small, it was found necessary in all cases to shunt across the galvanometer with a resistance r.

The following table gives an idea of the precision with which two capacities may be compared by this method.

R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
1,957.1	2,000	.2	.19571	1,927.9	1,970	.2	.19572
1,947.3	1,990	.2	.19571	1,918.0	1,960	.2	.19571
1,937.5	1,980	.2	.19571	1,908.3	1,950	.2	.19572

It will be noticed that the outstanding difference is about 1 part in 20,000 or .005 per cent., while for any particular setting, a change of 1 part in 100,000 could be easily detected.

The temperature coefficient of each subdivision of the capacity referred to was determined. The data for those parts showing the extreme variation is given in the table below.

Condenser.	Temp.	R_1	R_2	C_1	C_2	Temp. Coeff.
D	16	1,947.4	2,000	.05	.04868	
	24	1,945.5	2,000	.05	.04863	
	29.2	1,944.3	2,000	.05	.04861	
	33.3	1,943.1	2,000	.05	.04857	−.00011
B	16	1,999.6	1,982	.2	.20180	
	24	1,998.2	1,986	.2	.20123	
	29.2	1,994.7	1,986	.2	.20088	
	33.3	1,991.6	1,986	.2	.20061	−.00033

The temperature coefficients for the other parts of the capacity are between these values and are as follows: Capacity *A*, — .00018; *C*, — .00028; *E*, — .00013.

For convenience in plotting, all of the curves have been placed upon the same sheet. The ordinates at the left refer to curve *A*. For curves *B* and *C*, subtract .2815 and .2870. The ordinates at the right are for curve *D*. For curve *E*, add .00015 to these values.

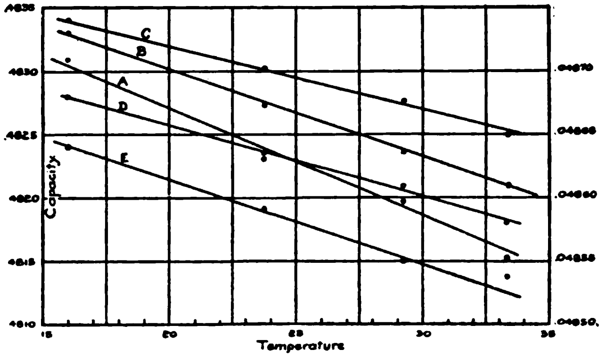

Fig. 3.

It will be noticed that all of the points lie reasonably close upon straight lines, with the exception of curve *E*. This condenser showed some leak, and it was impossible to obtain a perfect balance. The separate parts of the condenser taken as a standard were tested later and found to give values of the same order of magnitude.

In conclusion it would seem that a condenser has a temperature coefficient depending in value upon the construction, that it is negative, and of sufficient magnitude to require consideration when used in measurements of high precision.

PHYSICAL LABORATORY, UNIVERSITY OF WISCONSIN,
April 20, 1905.

NEW BOOKS.

Dynamics of Particles and of Rigid, Elastic, and Fluid Bodies. By A. G. WEBSTER. Leipzig, B. G. Teubner, 1904. Pp. xii + 588.

As one reads the title page of this recent work on dynamics, one has a feeling of regret that no American publisher should have had the honor of producing it, and at the same time, one of pleasure that the work of an American professor should appear in this distinguished series of books being published by the house of Teubner. Before saying anything in review of the book, it may not be out of place to express here the pleasure it is to have a book with such clear type, excellent paper and binding. The whole mechanical execution of the work is excellent.

As Professor Webster notes in his preface, most books on dynamics treat the subject in a purely mathematical standpoint and the subdivisions are made accordingly. Within recent years, however, it has been recognized that the science belongs primarily to physics and that no student in the latter science can properly understand it unless he has a firm foundation in dynamics, so that "the aim of this book is to give in compact form a treatment of so much of this fundamental science of dynamics as should be familiar to every serious student of physics." The standard treatises on dynamics and the allied subjects of elasticity and hydrodynamics are so extended in their treatment that it is practically impossible for any physical student, whose main purpose in life is experimental research, to read them, except in part. With this thought in mind Professor Webster has prepared the book under review and has included in it what, in his opinion, constitutes the essential features of the subject and has added whatever sections were necessary in order to prepare the student to read other books more advanced or more detailed.

"The work divides itself naturally into three parts, the first of which considers the laws of motion in general and those methods which are applicable to systems of all sorts." The separate chapters of this part include "Kinematics of a Point," "Laws of Motion," "General Principles (such as that of Virtual Work)," "Work and Energy," "Principle of Least Action," "LaGrange's Equations," "Oscillations and Cyclic Motions."

The second part is devoted to the "Dynamics of Rigid Bodies," and is divided into two chapters, one dealing with "Systems of Vectors, Moments of Inertia, Centrifugal Forces, etc."; the other, with the "Dynamics of Rotating Bodies."

"The third part divides itself from the other two from the fact that in it the differential equations are partial, and in the others they are ordinary." As a preparation for this subject there is a full discussion of the theory of the potential function, which introduces the most important mathematical theorems and prepares for the subsequent chapters. Next follows the "Dynamics of Stress and Strain," the "Statics of Fluids," the "Problem of de St. Venant on the Flexion and Torsion of Prisms," and "Hydrodynamics." In this last chapter there are but 62 pages but there is a most satisfactory treatment of both irrotational and vortex motion, of wave motion, and of viscous fluids. At the end of the book there are five notes dealing with mathematical difficulties which have arisen in various chapters.

From this brief outline one may form an idea as to the scope of the work, but it may be of interest to call attention to certain features which distinguish it from any other book on the subject. Professor Webster has succeeded most admirably in preserving the perfection of analytical treatment called for in the development of the various theorems, and at the same time, he has presented in a most interesting manner the physical interpretation of the various formulæ. He has described, for example, some interesting modifications of Maxwell's dynamical top, and has called attention to certain practical illustrations of important theorems, such as are afforded by naval torpedoes, crushing mills, etc. Whenever in the course of a problem a formula appears which has a practical application, attention is called to this fact. In short, as a textbook of mathematical physics, in which both sciences claim an equal share, this book of Professor Webster's is by far the most interesting that is known to the writer of this review. What gives additional charm to the present treatise is the introduction into the text of personal notes dealing with the history of various theorems and experiments. In fact, the book as a whole, quite apart from the most important considerations, forms most delightful reading, owing to the charm of the language, the arrangement of the matter, the selection of illustrations and the thoroughly practical tendency of the treatment.

It is natural that different people should view dynamics from slightly different points of view, and should have their preference for certain modes of treatment. It seems to the reviewer that in places Professor Webster has sacrificed clearness of physical ideas for the sake of mathematical exactness. For instance, in speaking of Foucault's pendulum and gyroscope, sufficient emphasis is not placed upon the physical interpretation of the equations; and, in fact, most of the phenomena could have been deduced from most elementary considerations. A more elementary discussion of flexure and torsion might well have been added. The proofs of the important mathematical theorems such as those of

Stokes, Gauss, etc., are all given in a satisfactory manner, although, personally, in some cases the reviewer prefers others. In all cases, however, the illustrations chosen are most admirable.

From time to time in reading the book one meets certain sections which from one cause or another are not perfectly satisfactory, and to which it may be only fair to call attention. For instance, in discussing small oscillations a most ingenious method is adopted for the determination of the nature of the roots of Lagrange's determinant. The proof as given certainly requires amplification by the discussion of the reality of the variables at the very beginning of the argument. In this same connection, when the final solution for the oscillations is given, the phases of the partial vibrations are all made equal without any statement as to the reason for it, other than one that if the solutions be substituted in the differential equations they will be satisfied. (This same somewhat summary mode of treatment is given also in Rayleigh's Theory of Sound.) Again, in the discussion of zonal harmonics and in an illustration of their application to the attraction of a homogeneous body symmetrical about an axis of revolution, a solution of the problem is written which certainly is *a* solution. It would seem to be necessary for the completion of the argument to prove that it is the only solution. In fact, however, in no book on mathematical physics known to the reviewer is there any attention called to the necessity for this addition to the proof of this or similar formulæ, and it may, therefore, be that the need of such an addition is simply a prejudice of his. In the treatment of stress and strain the value of the ratio of expansion due to the strain is given in its usual determinate form, but is deduced simply for the case of a *pure* strain, whereas, the same formula is used in the following pages for other strains which are not pure. A more general proof of the expansion formula might have been given equally as well.

In deducing the formula for the work done in producing strains it would be better to emphasize particularly the fact that the formula deduced is for a *change* in an existing strain. Again, in writing the formulæ for a simple shear as an illustration of equilibrium on page 461, it would have been better to have followed the same definition as on page 440 and thus to have avoided confusion.

These points of criticism are of minor importance obviously, for the general plan of the book is so good, the omissions are so few, the mathematical treatment is so clear and elegant, the physical illustrations are so well chosen, that this treatise is by far the best suited of all books known to the reviewer to be placed in the hands of physical students either in universities or in the higher grades of technical schools.

J. S. Ames.

The Becquerel Rays and the Properties of Radium. By Hon. R. J. Strutt. 8vo, pp. vii + 214. London, Edward Arnold, 1904.

Radioactivity: An Elementary Treatise from the Standpoint of the Disintegration Theory. By Fredk. Soddy. 8vo, pp. xi + 214. London, The Electrician Publishing Co., 1904.

Radioactivity. By E. Rutherford. 8vo, pp. ix + 399. Cambridge, The University Press, 1904.

Untersuchungen über die Radioactiven Substanzen. By Mme. S. Curie. Translated into German by W. Kaufmann. 8vo, pp. viii + 132. Braunschweig, Vieweg und Sohn, 1904.

Das Radium: Seine Darstellung und seine Eigenschaften. By Jaques Danne. 8vo, pp. 84. Leipzig, Veit & Co., 1904.

When we remember the almost unprecedented popular interest that has been aroused by the discoveries in the field of radioactivity it is a pleasant surprise to note how few sensational books have appeared on the subject. It is true that a few pamphlets of an objectionable character, and numerous newspaper articles, have been published. But the books on radioactivity are almost without exception of permanent scientific value. The scientific public also is to be congratulated on the fact that the authors of these books are usually themselves workers in this most interesting and difficult field, who speak of what they know at first hand, and to whose investigations the rapid development of the subject is in large part due.

None of the books here considered can be said to give a "popular" account of radioactivity, if by this is meant a treatment that would be intelligible to one with no knowledge of physics. In fact an account of this subject intended for one entirely ignorant of physics would have to be too superficial to be of much value. But for one who already has some knowledge of fundamental laws and principles and who wishes something more than can be obtained in the popular magazines, the admirable book of Strutt on "The Becquerel Rays and the Properties of Radium" will be found in the highest degree interesting and instructive.

Starting out with a chapter on the electric discharge in high vacua, — introduced in order to familiarize the reader with the cathode rays, the canal rays, and related matters, — the author develops the subject of radioactivity in a manner which is at the same time historical and logical. The book is written in an interesting and pleasing style. It is entirely free from mathematical methods, but rigorous and sound; written in a conservative spirit quite free from any suggestion of sensationalism, while at the same time doing full justice to the remarkable and intensely interesting features of the subject. Appendixes describe several simple experiments for illustrating the properties of radioactive substances; the theory of the deflection experiments with the β-rays; and a brief account of the methods of extracting radium from pitchblende. In its clearness and soundness as well as in its interesting style Mr. Strutt's book recalls the writing of Tyndal. It may be strongly recommended not only to the general readers for whom the author seems to have intended it, but also to scientific workers who have not found time to follow the extensive and somewhat confusing literature of radioactivity and now feel the need of a book that shall present the main facts, and their bearing upon scientific theories, with clearness and reasonable brevity. The fact that Mr. Strutt's book is the most recent of those here considered is also of some importance.

Those who wish to obtain a somewhat more detailed knowledge of the methods and results of the study of radioactivity, yet without making an extended study of the subject, will turn to Soddy's "Elementary Treatise on Radioactivity from the standpoint of the Disintegration Theory," the material of which first appeared as a series of articles in the London Electrician beginning in October 1903, and has since been suitably revised and expanded. The book is clearly written and has doubtless proven very generally useful. It has the disadvantage, in some accounts perhaps the advantage, of occupying an intermediate position among the books here considered; it contains so much that is beyond the experience of the general reader, that it cannot well serve as a popular account of the subject; while for those who wish to make a somewhat serious study of radioactivity the treatment is not sufficient in detail. The discussion of the significance of the various phenomena of radioactivity in their bearing upon physical theories is both interesting and suggestive. Especially is this true in the case of the last chapter—"Anticipations." The author's temerity in introducing a chapter of this kind is in part justified by recent developments, for in several instances the views advanced have been either wholly or in part confirmed.

It need hardly be said that the standard treatise on radioactivity is that of Rutherford; and it will doubtless remain so as long as the work is frequently revised so as to keep up with the rapid development of the subject. There are some perhaps, who would prefer to have a treatise of this kind so written as to be independent of any particular theory of the phenomena considered. But when we recall the prominent part taken by Rutherford in the development of the disintegration theory of radioactivity, we can scarcely expect a treatment of the subject in which this theory remains in the background; for, since the first and almost prophetic suggestion of Elster and Geitel, no one has done so much as he to develop the theory and to bring about its almost universal acceptance. Scarcely an example occurs to me of a theory that has been so altogether useful as this. It has not only been of immense assistance in guiding investigation, having led to the discovery of phenomena and laws which would otherwise have remained unsuspected, but its aid in the statement of phenomena has become almost indispensable. A writer who should attempt to give an account of the complicated phenomena of radioactivity now known, without the assistance of the concrete pictures furnished by the disintegration theory, would find that he had on his hands a very difficult undertaking. The author says in this connection: "The phenomena exhibited by the radio-active bodies are extremely complicated, and some form of theory is essential in order to connect in an intelligible manner the mass of experimental facts that have now been accumulated. I have found the theory that the atoms of the radio-active bodies are undergoing spontaneous disintegration, extremely serviceable not only in correlating the known phenomena, but also in suggesting new lines of research. The interpretation of the results has, to a large extent been based on the disintegration theory, and the logical deductions to be drawn from the application of the theory to radio-active phenomena have also been considered." Professor Rutherford's treatise will be consulted by those who seek a thorough and detailed account of methods and results in the field of radioactivity; by those who wish to find references to original articles in this field, for the citations to the literature of the subject are wellnigh complete; by those wishing an authoritative account of the development and present status of the disintegration theory; in fact by every one who has need of a *treatise* on radioactivity, rather than a popular or semi-popular account. Special reference should be made to the very useful chapters on the "Ionization Theory of Gases" and "Methods of Measurement." Strange to say no other book with which I am acquainted contains a really usable account of the experimental methods used in the study of radioactivity.

The three books thus far considered, while differing widely in other respects, have one feature in common: the phenomena are interpreted in each case from the standpoint of the disintegration theory. All three books represent the British school of radioactivity, if we may use the term. In the earlier books by Madame Curie and by Danne we have the French school represented. Madame Curie's book will always have a peculiar interest of its own, which will persist even after the subject has progressed to such an extent that the value of the book is chiefly historical. That time, however, has not yet come. Madame Curie's account of the work that led to the discovery of radium, and of the properties of radioactive substances, will still be found not only interesting but instructive. The experimental results are stated, usually in a brief style, without any attempt at interpretation and without preference for any theory. The disintegration theory has been of immense value in the study of radioactivity, and doubtless represents the nearest approach to the truth that has yet been reached. Nevertheless to consider the phenomena at times simply as phenomena and not in the light of any theory, is very useful, and will help to prevent one from falling into a rut. It is interesting also to see the subject in the different perspective which results from taking the French rather than the British viewpoint.

The little book by Danne, entitled "Radium, its Preparation and Properties," goes into the chemical side of radio-activity, especially in the case of the extraction of radium from its ores, more fully than any other book with which I am familiar. The discussion of the physical properties of radium, however, although clearly presented, is much briefer and less complete than that contained in the books already mentioned.

The minor part played by the chemical side of radioactivity in the books here considered is significant and calls attention to an unfortunate condition of affairs, which, unless it is remedied, will seriously retard further progress in this most important field. The study of radioactivity thus far has been almost wholly from the physical side, and in the great majority of cases has been carried on by physicists; the chemistry of the radioactive elements and their compounds, and the chemical aspects of radioactivity in general, have scarcely been studied at all. The development of the processes used in the extraction of radium from its ores and the discovery of the evolution of helium form almost the only exceptions to this statement. The excuse usually urged for this condition of things, namely the rarity and expense of the more strongly active substances, does not seem to me a good one. It is true that the rarity of radium prevents the employment of ordinary chemical procedure in its study. But new conditions require new methods. If Madame Curie had adhered solely to the methods of orthodox chemistry the new element would not have been discovered. It appears to me that the subject of radioactivity has reached a point where further progress will be slow unless aided by the effective coöperation of both physics and chemistry.

In none of the books here considered are the experiments with radioactive substances in the fields of medicine and biology adequately treated.

ERNEST MERRITT.

Handbuch der Spectroscopie, Band III. By H. KAYSER. S. Hirzel, Leipzig, 1905. Pp. viii + 604.

The third volume of Kayser's Handbook of Spectroscopy fulfills the promise of the earlier volumes as regards completeness and thoroughness of treatment. The present volume deals exclusively with absorption spectra and includes not only all that has been amassed by an army of investigators concerning the selective absorption of the visible rays but likewise all that has thus far been learned by the use of photographic methods concerning absorption in the ultra-violet spectrum and by means of the thermopile, bolometer and radiometer concerning absorption in the infra-red. Unfortunately the extensive explorations of the infra-red spectrum made by W. W. Coblentz were not completed in time to be included as a whole in Professor Kayser's Compendium, but his results in so far as they had appeared up to the middle of the year 1904 are included.

Chapter I. of the present volume deals with the apparatus and methods for the study of absorption and Chapter II. with variations in absorption spectra and the influence of temperature, pressure, etc., upon the same. Chapter III. which was written by Professor Hartley of Dublin, deals at great length with the difficult question of the relations between the absorbing power and constitution of organic compounds. The remainder of the volume consists of a systematic summary of the absorption of the various elements and their compounds with an alphabetical descriptive list of all known absorption spectra together with references to the original sources from which the data have been derived. E. L. N.

Modern Theory of Physical Phenomena. By AUGUSTO RIGHI. Translated by AUGUSTUS TROWBRIDGE. 8vo, pp. ix + 165. New York, The Macmillan Co., 1904.

The eight years that have elapsed since the introduction of the electron into physical theories have witnessed changes of a most fundamental and far reaching character in our manner of interpreting physical phenomena. While it is to the study of the cathode rays that we owe the first experimental evidence of the existence of charged particles smaller than atoms, the utility of the electron in physical theory has not been confined to the phenomena of the discharge in gases, nor even to the discussion of phenomena of a purely electrical character. There is now not a department of physics left in which the modern conception of electrons has not played a part. In some cases it has led to new theories; in others it has made possible the statement of old theories in new and more concrete form. For one who wishes to remain in touch with the rapid developments of physics a knowledge of the fundamental notions of the modern electron theory is therefore absolutely essential.

It is the purpose of Professor Righi's excellent book to give this knowledge of the fundamental notions. The book is non-mathematical; only rarely does an algebraic or geometrical discussion appear in a footnote, and always of the simplest character. Beginning with a consideration of ordinary electrolysis the author then considers the Zeeman effect, cathode rays, conduction in gases and solids, radioactivity, and finally the constitution of matter. The treatment is brief, but remarkably clear. In so small a book no detailed discussion of the many topics treated can be expected. But the outline is given, and with it and the suggestion that there is more to the subject than is contained in this book. References to original articles are frequent. The translation from the Italian, undertaken by Professor Trowbridge with the coöperation of the author, is highly satisfactory.

Although Professor Righi himself has carried out numerous important investigations along lines closely related to electron theory, it cannot be said that much of the work leading to the development of this subject has been done in Italy. In the opinion of the reviewer this fact adds to the value of a book like that here considered. The subject is presented to us by one who sees it from the outside. The treatment is appreciative, but at the same time conservative; and there is none of the faulty perspective, resulting from unrestrained enthusiasm, which is sometimes seen in similar books by English authors.

Ernest Merrit.

The Recent Development of Physical Science. By William Cecil Dampier Whetham. 8vo, pp. xii + 344. Philadelphia, P. Blackiston's Son and Co., 1904.

In modern scientific investigation coöperation between different related branches of science is becoming more and more essential. Each investigator is a member of the great scientific army that is battling with the unknown. In modern warfare individual companies and regiments do not fight alone, but each part of the army keeps itself informed of the progress made by the rest, so that an advantage gained by one may be utilized by all.

It is the recognition of this need of scientific coöperation that has led to the preparation of Mr. Whetham's book. The author says: "Thus it happens that an acquaintance with the knowledge newly acquired in one department of science is necessary for the study of another; indeed, the phenomena which need for their interpretation the methods of two branches of science have proved often the most fruitful field of inquiry. For reasons such as these it has been thought possible that a short account of some of the important investigations now being carried on in the physical laboratories of the world might be useful to students of science in general; while it is hoped that, by treating the subjects as far as possible without technical language, the book may also appeal to those who, with little definite scientific training, are interested in the more important conclusions of scientific thought."

It will be seen that the general purpose of the book is the same as that of Righi's "Modern Theory of Physical Phenomena." But while the latter book deals only with the various phases of the electron theory, the former covers a far wider field. The scope of the book is indicated by the following list of topics treated: The Philosophical Basis of Physical Science; The Liquefaction of Gases and the Absolute Zero of Temperature; Fusion and Solidification; The Problems of Solution; The Conduction of Electricity through Gases; Radioactivity; Atoms and Ether; Astrophysics.

The attempt to cover so much ground unfortunately results in a less thorough treatment of the topics considered than that of Righi. References to original sources are absent. Occasionally the statements made are misleading, either because of their brevity or actual inaccuracy. Take for example the interpretation put upon the negative Joule-Thomson effect in hydrogen, which the author ascribes to a force of repulsion between the hydrogen molecules. Later the reversal of the effect at —80° C. is mentioned, and will naturally be interpreted by the reader as indicating a change at that temperature from molecular repulsion to molecular attraction. One who is prepared to read the chapter on the liquefaction of gases understandingly will not look with favor upon a theory that requires such an assumption as this, — an assumption that was perhaps natural enough fifty years ago, but which is now no longer necessary.

A misleading statement of another kind appears in the chapter on conduction through gases, where the author says that "the effect of very high vacua on the electric discharge was first systematically investigated by Sir William Crookes." To those who are familiar with the classical articles of Hittorf, whose publication preceded the work of Crookes by several years, and which contain descriptions of phenomena that are even now being rediscovered, such a statement seems unfortunate.

In trying to make the same book serve for the two classes of readers referred to in the preface — namely the educated man who has a general interest in science, and the scientific worker in other fields, — the author has undertaken a very difficult task. In fact it appears to me almost impossible to carry out such an undertaking so that the result shall be satisfactory from both points of view. Some lack of exactness is inavoidable in a popular account of scientific work, and even a certain amount of carelessness in statement is excusable, although regrettable. But in a book intended for workers in other branches of science — men who have scientific training and the scientific instinct, but whose work has simply been along other lines — any carelessness in the presentation of what is to the reader a novel theory is apt to diminish the value of the book very greatly. It must be remembered that many hypotheses or modes of thought to which the physicist has become accustomed may appear in an entirely different light to workers in other fields. A book written for such an audience has failed in its purpose unless it gives to its readers an understanding of the reasons which have led to the adoption of new hypotheses.

In some cases I think that Mr. Whetham's book has failed in just this way. Consider for example the hypothesis that lies at the foundation of all branches of the electron theory — the assumption of the existence of portions of matter smaller than atoms. This assumption is introduced in the chapter on conduction through gases in an offhand way, natural perhaps to one long familiar with the, at first, startling suggestion. Later there is indeed an attempt to give the reasons for believing that corpuscles are smaller than atoms. But the discussion appears to me entirely inadequate. It really makes the whole argument rest on the results of J. J. Thomson's determination of the charge carried by an ion in air. The results of these experiments are certainly interesting, and are important when taken in connection with the great mass of indirect evidence pointing in the same direction. But when one remembers the number of questionable assumptions that are involved in the determination, no one would be willing to accept the conclusion on such evidence alone. Certainly the chemist, who sees in the electron hypothesis a contradiction of laws which he has long regarded as fundamental, will not be converted to the new theory by such a presentation of the case. To make the book of value to such readers the author should have borne in mind the skeptical attitude held by most physicists only a few years ago, and should have indicated the steps by which accumulating experimental evidence virtually forced the acceptance of the electron theory.

There are numerous instances where criticism similar to that above might properly apply. The reviewer feels that the author has had the opportunity to supply a book whose need is strongly felt; but that the opportunity has not been fully utilized. The book is written in an interesting style, however, and contains much that it would be difficult to find in better form elsewhere. The essential fault that one finds in the book is not that it is bad, but that, although good, it might have been so much better.

Ernest Merritt.

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THE

PHYSICAL REVIEW.

ON THE SPECIFIC HEAT OF GASES AT HIGH TEMPERATURES.[1]

By L. Holborn and L. W. Austin.

THE specific heat of gases at constant pressure was first successfully determined by Regnault.[2] His observations covered the temperature interval from — 30° to + 210° C. and pressures from 1 to 12 atmospheres. He found that the specific heats of the simple gases, air, oxygen and hydrogen were independent both of temperature and pressure within the limits of the observations. The specific heat of carbon dioxide, on the other hand, when measured between 0° and 200° showed a well marked increase with increasing temperature.

E. Wiedemann,[3] who repeated the experiments of Regnault on a smaller scale, arrived at similar conclusions. Witkowski,[4] investigating air at low temperatures, between 100° and — 170°, also found the specific heat constant. On the other hand he found that it increased with increasing pressure (up to 70 atmospheres) and that this increase rose with decreasing temperature. An increase of specific heat with increasing pressure has also been observed by Lussana[5] between 0° and 200° in the case of air, oxygen and carbon dioxide.

[1] Translated from Abhandlungen der Phys.-Tech. Reichsanstalt, Vol. IV., Heft. 2, p. 133, 1905.

[2] V. Regnault, Relation des exper., 2, 1862.

[3] E. Wiedemann, Pogg. Ann., 157, p. 1, 1875.

[4] A. Witkowski, Journ. de phys. (3), 5, p. 123, 1896.

[5] S. Lussana, Cim. (3), 36; (4), 1, 3, 6, 7, 1894–98.

The specific heat at constant volume has been measured by Joly[1] who enclosed the gases (air, hydrogen and carbon dioxide) under high pressure in hollow copper spheres and determined their specific heats between room temperature and 100° by means of the steam calorimeter.

In addition, the mean specific heat at constant volume between 0° and a high temperature has been measured by means of explosion experiments, by Mallard and Le Chatelier[2] (1300° to 2800°), by Berthelot and Vieille[3] (2800° to 4400°) and recently by Langen[4] (1300 to 1700°).

METHOD OF OBSERVATION.

All the observers who have measured the specific heat at constant pressure have made use of the method of mixtures of Delaroche and Berard.[5] The gas first flows through a tube system surrounded by a bath of some liquid where it is heated to the desired temperature, and finally flows out through a second tube system surrounded by the water of the calorimeter where its heat is given up. The temperature at which the gas enters the calorimeter is determined by means of a thermometer in the heating bath, and the temperature at which it leaves is given by the thermometer in the calorimeter, experiments having been made to show that the gas actually assumes the temperatures of the heating bath and of the calorimeter as it passes through them.

The connection between the heating bath and calorimeter must be made as short as possible in order that the gas may enter the latter with the least possible loss of heat in transit. There is, however, always a heat loss at this point, the influence of which can be made negligible only by using powerful gas currents. Regnault took great pains in the investigation of this source of error. In his experiments with air he varied the flow of gas between wide limits increasing it until the value of the specific heat became independent of the quantity per minute. In the calculation of the specific heat a correction must be made to the observed rise in temperature of the calorimeter. This is due partly to the radiation of the calorimeter and partly to the heat conducted to it from the heating bath through the connecting tube. The first portion, which is common to all calorimetric measurements, can be controlled by choosing a suitable initial temperature for the calorimeter, while the second can be kept within the necessary bounds by introducing bad conducting material in the connection between the calorimeter and heater. By observing the course of the calorimeter temperature before and after the passage of the gas this correction is determined. It is nevertheless doubtful whether with the Regnault arrangement the flow of heat due to conduction does not change when the gas current sets in. The question can be investigated only indirectly, by varying the strength of the gas flow.

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[1] J. Joly, Phil. Trans. (A), 182, p. 73, 1891; 185, pp. 943 and 961, 1894.

[2] Mallard and Le Chatelier, Ann. des mines (8), 4, p. 274, 1883.

[3] Berthelot and Vieille, Ann. de chim. et de phys. (6), 4, p. 13, 1885.

[4] Langen, Forschungsarbeiten, herausgegeben vom Ver. Deutsch. Ing., Heft 8, p. 1, 1903.

[5] Delaroche and Berard, Ann. de chimie, 85, p. 72, 1813.

Witkowski varied the above method of measuring the gas temperature by making use of a thermoelement protected from radiation, which could be brought close to the opening of the calorimeter. In the present investigation which has for its object the determination of the specific heats at high temperatures this method has also been used. For the heating of the gases however baths were discarded as they are not convenient above 500°.

ARRANGEMENT OF APPARATUS.

The Heating Tube. — The gas was heated electrically in a nickel tube *A*, 1.2 m. long 8 mm. inner diameter, and of 1 mm. wall thickness, on which was wound a coil of nickel wire. The windings were insulated from the tube by asbestos and from each other by clay put on wet. Outside this was a second layer of asbestos, and the whole was inclosed in a porcelain tube. The gas was introduced at one end and was heated in the coarse nickel filings with which the tube was filled according to the plan of E. Wiedemann. At three-fourths the length of the tube it encountered a dividing wall soldered in with silver and was led out through a side tube 25 mm. long and 4 mm. in diameter into the calorimeter. In this way the influence of the cool end of the tube was eliminated. Otherwise the gas in passing through the cool portion gives up so much of its heat that its temperature varies in a marked degree with the strength of the flow.

Opposite the outlet tube *W* a second nickel tube *B* (25 cm. long, 4 mm. diameter) was joined to the heating tube and through this a platinum platinum-rhodium thermo-element *T* was introduced. This passed through the heating tube *A* which at this point was kept free from nickel filings by the dividing wall *M* on one side and a disk of wire net on the other. The thermojunction lay in the outlet tube *W*, 1 cm. from its free end. In this space a thin silver band bent in the form of a screw was inserted to prevent radiation of the thermojunction to the cool calorimeter. The thermoelement consisted of wires 0.25 mm. in diameter which were insulated through

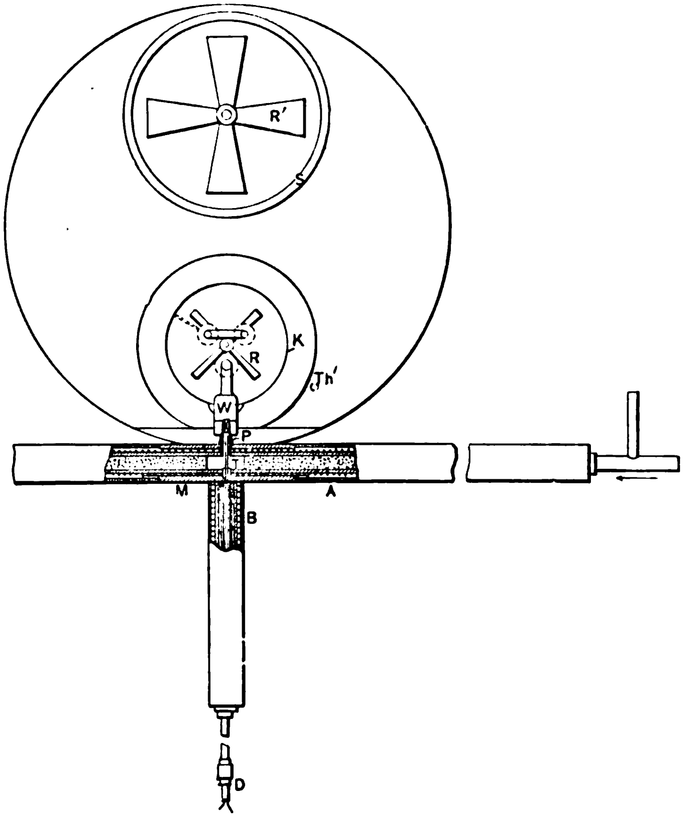

Fig. 1.

the greater part of tube *B* with thin porcelain tubes. In the portion near *A*, in *A* itself and also in *W*, the insulation consisted of thin quartz capillaries lying close together and wrapped about with platinum band 0.01 mm. in thickness. The thermojunction which was hardly thicker than a single wire was free from quartz and was nsulated from the platinum sheath by an air space. Special car was taken that the end of the thermoelement should not come in contact with the tube wall. In one portion of the work this was

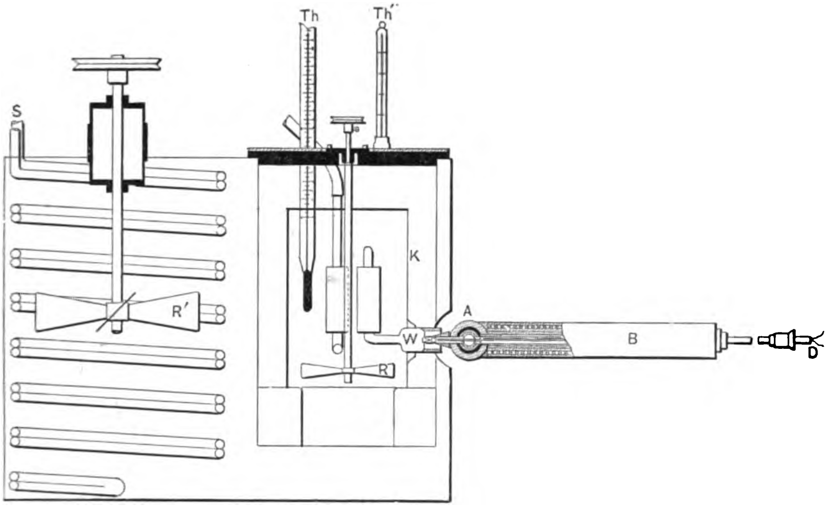

Fig. 2.

attained by supporting the flexible end of the element on a bit of mica of the same width as the diameter of the tube. The platinum band which was intended for the protection of the thermoelement from radiation from the tube wall also served to protect the quartz from the nickel oxide which was carried along with the gas current in minute quantities from the heating tube. Otherwise this after a time became opaque and disintegrated.

The wires of the thermoelement were insulated from the tube *B* by a porcelain tube which passed out through a rubber stopper at *D*, in which it could be moved back and forth when it was desired to determine the temperature at different points in the tube *W*. The end *D* of the tube always remained cold enough so that the wires could be sealed into the end of the porcelain tube with sealing wax.

A secondary heating coil of nickel wire wound on porcelain 12.5 cm. long and insulated like the main coil was placed on the tube *B* to compensate for the loss of heat by conduction through the two side tubes and for the loss of one turn of wire on the main coil where the side tubes were attached.

The Calorimeter. — The calorimeter *K* of about 0.5 liter capacity was made of pure silver 0.5 mm. thick (Figs. 1 and 2). In its center were situated three silver tubes 1.5 cm. in diameter filled with silver filings and connected by 0.6 cm. silver tubes. These absorbed the heat from the gas as it passed through. That the gas actually issued from the calorimeter at calorimeter temperature even when heated to the highest point (800°) was made certain by experiments with a constantan copper thermoelement.

A thermometer *Th* with inclosed scale divided in 0.1° and read by means of a telescope served for the measurement of the specific heat. A small stirrer *R* insured the rapid and regular taking up of the heat of the silver tubes by the water. The weight of the calorimeter including the tubes and filings was 247 g.

The calorimeter was surrounded by a copper water jacket and was placed at one side instead of at the center of this in order that the heating tube might be brought as close to the calorimeter as possible. The water jacket had a capacity of 15 liters. The temperature of this tended to rise slowly due to the radiation from the heating tube. To obviate even this slow change a spiral tube was introduced into the jacket through which cold water from the house system flowed. The quantity of water required for any given heating tube temperature was regulated according to the readings of a water manometer. By this means the jacket temperature indicated by the thermometer *Th'* was kept constant during the time required for an experiment to 0.1°. This temperature was generally about 18°. The water in the jacket was stirred by a stirrer *R'* driven by the same electric motor used for driving the calorimeter stirrer *R*.

In former researches the connection between the calorimeter and heating apparatus was made by means of cork. This material is not usable however much above 200°. In our work the means of connection consisted of a specially made porcelain tube shown in natural size in Fig 2, *a*. The larger end of this was inserted in the mouth of the system of tubes of the calorimeter while the other end fitted over the tube *W* reaching as far as the windings of the heating tube *A*. Both the joints were made tight by firmly packed asbestos.

The Gases. — The gases for the investigation were taken directly from ordinary commercial cylinders. Before entering the heating tube the gas passed through a glass tube 1.5 m. long filled with calcium chloride. The strength of the gas stream was regulated with sufficient accuracy by means of an ordinary reducing valve, the pressure read on a mercury manometer before the gas entered the heating tube, remaining constant to 1 mm. Only in the case of carbon dioxide was it found necessary to regulate during the experiment. This was evidently due to the changes in the valve temperature resulting from the evaporation of the liquefied gas. The gas entered the heating tube *A* under an excess pressure of about one-half atmosphere which was necessary on account of friction on the nickel filings which increased with the temperature. For overcoming the friction in the system of tubes in the calorimeter only a pressure of from 1 to 2 cm. of mercury was required, as was established by special experiments. No heat due to the friction of the gas on the filings in the calorimeter was observed.

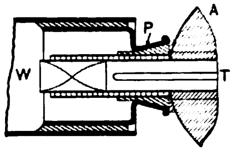

Fig. 2, *a*.

The Gasometer. — The quantity of gas was measured after it left the calorimeter. The gasometer which served to hold and measure the gases is represented in Fig. 3. The gas passed first through a spiral cylinder S_1 and then entered a rubber bag *G* which hung in a closed zinc cylinder. From this a quantity of air, equal in volume to the gas entering the rubber bag, was forced through the tube *L* into the vessel *F* out of which water was expelled through the opening *Q*. This was caught in a pail and afterwards weighed. By this arrangement gas left the calorimeter under a constant pressure differing only a little from the pressure of the atmosphere. The presence of the rubber bag guarded against the possibility of absorption by the water, of the gases measured, since only the air from the zinc cylinder came in contact with the water. There was no difficulty in determining the volume of CO_2 with this arrangement as the diffusion of this gas through the rubber during the short time required for an experiment could be neglected.

The zinc cylinder *Z* and the vessel *F* were kept at the same temperature. To this end the cylinder was placed in a large bath the water of which was continually renewed from the water system of the laboratory, while the vessel *F* which was surrounded with a layer of cotton covered with oil cloth, was filled through the funnel *N* from the same source before each experiment.

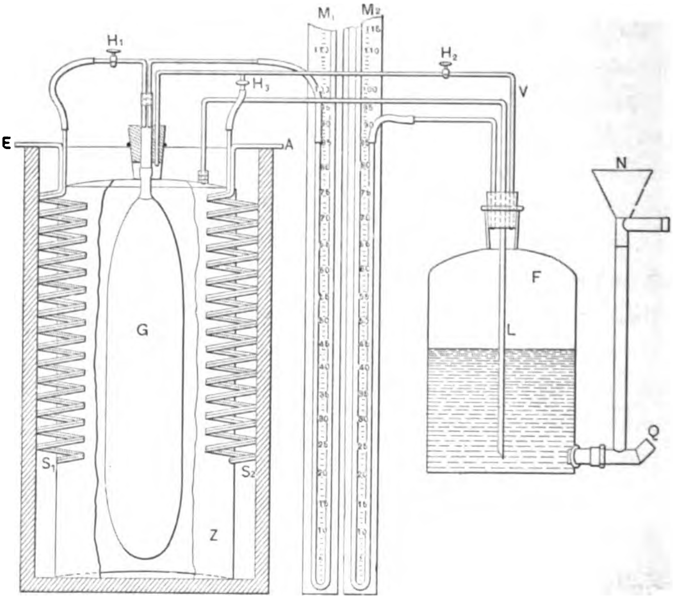

Fig. 3.

Since the gas passed through the copper spiral S_1, situated in the same bath with the zinc cylinder *Z* before entering the rubber bag, it was not necessary to wait long for it to attain the bath temperature. This otherwise would have consumed considerable time as the quantity of gas was usually about 20 liters. Before the first experiment each day it was necessary to wait for some time after filling the bath until the air in the zinc cylinder had completely assumed the bath temperature. This never varied more than 1° during the day.

After each experiment the air was generally forced back from the vessel F into the cylinder Z. This was accomplished by closing the opening Q and the cock H_3 and opening H_2 and H_1. Water was then poured in through N, and the air passed through the tube V and at the same time forced the gas from the rubber bag out through H_1. Air could be introduced into the zinc cylinder also through the cock H_3, being brought to the temperature of the bath by passing through the spiral S_2. Ordinarily this opening was used only to bring Z to atmospheric pressure. The pressure of the gases in G and F was read on the water manometers M_1 and M_2. G was brought to atmospheric pressure before each experiment and again after the entrance of the gas. This was accomplished after the closing of the cock H_1 by opening H_2 for a moment so that a little air flowed from Z to F through the tube V.

Letting M denote the weight of the displaced water in kgs., T its temperature (which differed only a fraction of a degree from the temperature of the zinc cylinder), H the pressure (mm. Hg) in the vessel F, which was given by the readings of the barometer and the manometer M_2, the mass m (in grams) of the gas contained in the rubber bag is

$$m = M \frac{H}{760} \frac{s}{1 + \alpha t},$$

where α is the expansion coefficient and s the weight (in grams) of 1 liter of gas at 0° and 760 mm.

The Gas Temperature. — The temperature of the gas was measured just before it entered the calorimeter with the thermoelement already described. Details regarding its use have been given in a former paper by one of the authors.[1] For the sake of certainty new wires were made use of since those which have been already used immersed to a considerable depth in a heated region sometimes cease to be homogeneous in the neighborhood of the junction. This can easily lead to errors when, as in the present case, the wires are heated only close to the junction.

After many preliminary experiments in which among others the thermoelement was surrounded by a silver tube insulated from the walls of the tube *W* through which the gas entered the calorimeter, we finally heated the tube *W* by means of a coil of 0.2 mm. platinum wire. This was wound on a thin layer of asbestos paper in bifilar winding so that the two free ends came out together from the porcelain tube *P* close to the heating tube *A*. Toward the calorimeter the windings were brought closer together so as to produce as nearly as possible a uniform temperature throughout the tube *W*. The current in the platinum coil was regulated so that the thermojunction indicated the same temperature of the flowing gas when it was displaced to different points along the tube *W*. Then, since in the actual measurements the junction always lay close to the screw-shaped silver plate, it followed that as soon as the gas flowed the whole of the thermoelement was at the same temperature as far as the point where it entered the tube *B*. Before and afterward the readings were lower, but rose at once as soon as the cock of the gas cylinder was opened, and remained constant in general during the whole time that the gas flowed. Only in the case of the highest temperature was there a slight fall when the flow continued for some time, evidently caused by the fact that the heating tube *A* did not have sufficient heat capacity and gradually cooled during the course of the experiment.

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[1] L. Holborn and A. Day, Ann. d. Phys. (4), 2, p. 538, 1900.

The temperature of the gas as measured in this way before its entrance into the calorimeter, is exactly determined by the condition of the heating tube. Within wide limits it is independent of the quantity of gas flowing in unit time, when the same current is sent through the heating coils. The kind of gas is also of little influence. Even at 800° carbon dioxide gave only about 6° lower temperature than air and nitrogen. If it is desired only to compare[1] the specific heats of different gases at the same temperature, if we assume that the known specific heat of one of the gases does not vary with the temperature, the thermoelement could be removed and the temperature be determined by the change in calorimeter temperature produced by the passage of the standard gas. It is then only necessary to keep the strength of the heating current constant and to regulate the quantities of the other gases so that each imparts about the same quantity of heat to the calorimeter.

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[1] E. Wiedmann made measurements on the specific heat of different gases above 100° in a similar way, heating his heating tube in an air bath and assuming that air remained constant between 20° and 200°.

It was found also that the ratio of the specific heats of the different gases was the same when the above mentioned silver tube was used and the side tube *W* not heated. The Regnault arrangement was also tried with success for measurements of this kind at 220°. From all this it is seen that an electrically heated tube for heating the gas can completely take the place of liquid baths, and that it is superior in ease of adjustment and constancy and in being applicable to higher temperatures. The only disadvantage is that the electric oven has a small heating capacity, this being about the same as that of an air bath. The current for the coil of tube *A* was taken from a battery of accumulators the voltage of which could be varied as desired. The coil *B* was in a shunt which in the beginning had to be regulated for each temperature. The small coil on the side tube *W* was connected to a battery of small accumulators and the current for each temperature regulated in preliminary experiments.

The amount of gas which could be used in each experiment was limited by the capacity of the gasometer, which was about 25 liters. Since carbon dioxide has the greatest specific heat per unit volume, it was used in the experiments for determining the dependence of the results on the velocity of the gas current. This influence was found to lie within the limits of the errors of observation. Ordinarily the gas was allowed to flow for four minutes, and the quantity was frequently increased or diminished by increasing or diminishing the velocity.

The Calorimeter Temperature. — The heat which the calorimeter received from without, coming for the most part from the heating tube through the small tube used for introducing the gas, necessitated a correction which was determined in the usual manner from observations on the change of temperature in the calorimeter for periods of ten minutes before and after the experiment. The readings on the thermometer in the calorimeter, which were always taken with rising temperature, lay between 3° below the water jacket temperature and about 10° above it. For our purposes it is allowable within these limits to make a linear interpolation of the correction during the time required for the experiment itself. We proved this both by plotting a curve for the correction from readings extending over the whole range of temperature, and also by imparting a definite amount of heat per unit time to the calorimeter from an electrically heated coil immersed in the water, beginning with different initial temperatures. The temperature of the heating tube was about 450° and the rise in the calorimeter temperature in the first and last periods varied between 0.13° and 0.06° per minute. During four minutes current was sent through the coil in the calorimeter so that the temperature rose about 4°, first at a mean calorimeter temperature of 19°, and then at 25°. The difference between the two results was on an average less than 0.2 per cent. In these experiments the calorimeter was slower in changing its temperature than in the experiments with gases where of course the small heating coil was absent. This, on account of the insulation of the wires, gave up its heat more slowly than the silver tubes. The cooling of the heated calorimeter before a new experiment was accomplished as follows: The water was first completely sucked out through the opening left for the thermometer. As the bottom of the calorimeter was curved all the water could be removed except that adhering to the walls. Then a fresh quantity of water of suitable temperature measured at 15° in a half-liter flask, was poured in. Before the calorimeter was connected to the heating tube it was proved by weighing that this procedure insured the constancy of the quantity of water to about 0.1 gram. The water equivalent of the calorimeter with its stirrer (except the portion above the glass insulator set in the spindle just above the calorimeter) and thermometer was 15.7 grams. The quantity of water was 499.6 grams so the sum

$$w = 515.3 \text{ g}.$$

Calling m the weight in grams of the gas entering the calorimeter, with the temperature θ_1, and ϑ' the resulting rise in temperature of the calorimeter, which is derived from the observed change in temperature ϑ by applying the correction k due to the heating by conduction, etc., and calling c the mean specific heat of the gas at constant pressure, and θ_2 the mean calorimeter temperature during the passage of the gas, then

$$w\vartheta' = cm(\theta_1 - \theta_2).$$

OBSERVATIONS.

The observations contained in the following tables were taken at three different temperatures of the heating tube, t_0 denotes the temperature of the calorimeter jacket, z the time of passage of the gas in minutes, τ_1 and τ_2 the mean change in the calorimeter temperature per minute during the periods before and after the passage of the gas. The order in which the observations were taken is shown by the dates.

It was in general so arranged that each gas was experimented upon at different times as a test of the constancy of the apparatus This was necessary inasmuch as the apparatus was several times taken apart, the insulation of the thermoelement renewed, and its junction often moved forward and back in the region of uniform temperature already mentioned. The differences were naturally smaller when the apparatus remained undisturbed. Changes in the gas temperature on the same day were generally caused by gradual decrease in the current strength in the heating coils. The increase in the calorimeter temperature ϑ is always calculated for one minute longer than the time of passage of the gas. The slower rise of temperature due to conduction from the heating tube, etc., set in regularly within one half minute after the gas ceased to flow. The regulating valve and mercury manometer allowed the gas current to be kept so constant that the temperature of the calorimeter rose regularly during the passage of the gas, which was clearly shown by the thermometer readings taken every half minute. Before and afterwards the thermometer was read each minute.

Observations were taken at three different gas temperatures, that is at 440°, 630° and 800°. An upper limit was placed to this temperature by the danger of melting the silver soldering of the nickel tube, and a lower limit by the uneven distribution of the temperature in the heating tube and the decreased sensibility of the thermoelement. The use of the same calorimeter for a given quantity of gas is advantageous only for a limited interval of temperature.

Oxygen was the least pure of the gases used. According to the analysis of the chemical laboratory of the Reichsanstalt it contained 9.5 per cent. (by volume) of nitrogen. Any change in the

Mean Specific Heat between 20° *and* 440°.

1904	t_0	z (Min.).	m (g)	Θ_1	Θ_2	ϑ	τ_1	τ_2	k	ϑ'	c
						Nitrogen.					
Aug. 24.	18.3°	4	22.90	441.8°	19.4°	4.951°	0.1084°	0.0755°	0.441°	4.510°	0.2403
	18.3	4	22.53	442.1	25.1	4.659	0.0720	0.0385	0.249	4.410	0.2419
Sept. 12.	18.1	3	21.44	444.5	18.9	4.650	0.1105	0.0665	0.332	4.318	0.2438
	18.2	3	21.49	444.7	24.5	4.458	0.0751	0.0413	0.216	4.242	0.2421
	18.0	4	24.62	444.8	18.8	5.376	0.1120	0.0718	0.439	4.937	0.2426
	18.0	4	24.73	444.8	25.0	5.080	0.0702	0.0284	0.226	4.854	0.2409
						Air.					
July 4.	18.1	4	22.44	443.0	18.9	4.821	0.1136	0.0764	0.456	4.365	0.2363
	18.1	4	22.56	444.2	24.6	4.668	0.0757	0.0458	0.289	4.379	0.2384
	18.0	4	21.44	443.4	18.7	4.615	0.1120	0.0766	0.454	4.161	0.2355
	18.0	4	21.61	444.2	24.1	4.471	0.0760	0.0472	0.294	4.177	0.2371
Aug. 24.	18.2	4	22.64	441.7	18.6	4.858	0.1104	0.0784	0.456	4.402	0.2368
	18.2	4	23.74	442.2	24.4	4.828	0.0772	0.0420	0.298	4.530	0.2354
						Oxygen (with 9.5 Per Cent. N.).					
Sept. 12.	18.0	4	25.08	444.4	18.7	5.115	0.1119	0.0741	0.446	4.669	0.2253
	18.0	4	25.63	444.2	24.6	4.935	0.0727	0.0341	0.238	4.697	0.2250
	18.0	3	22.24	445.2	19.2	4.480	0.1094	0.0716	0.343	4.137	0.2250
	18.0	3	22.84	445.3	23.8	4.421	0.0715	0.0313	0.185	4.236	0.2267
						Carbon Dioxide.					
Sept. 10.	17.9	3	28.28	442.8	19.1	5.712	0.1113	0.0679	0.337	5.375	0.2312
	17.9	4	26.31	442.8	25.4	5.124	0.0674	0.0219	0.201	4.923	0.2310
	18.0	4	25.00	443.6	19.2	5.139	0.1092	0.0703	0.429	4.710	0.2287
	18.0	3	28.29	441.7	25.2	5.457	0.0695	0.0250	0.167	5.290	0.2313
	18.0	4	29.57	442.8	19.3	6.006	0.1129	0.0678	0.429	5.577	0.2295
	18.1	4	32.54	441.7	26.2	6.228	0.0672	0.0160	0.182	6.046	0.2310

Mean Specific Heat between 20° and 630°.

1904	t_0	s (Min.).	m (g)	Θ_1	Θ_2	ϑ	τ_1	τ_2	k	ϑ'	c
					Nitrogen.						
Aug. 25.	18.1°	4	21.27	636.0°	21.4°	6.897°	0.1603°	0.1110°	0.654°	6.243°	0.2461
	18.1	4	21.21	638.4	21.0	6.884	0.1637	0.1141	0.668	6.216	0.2446
	18.0	4	19.72	637.4	21.0	6.456	0.1606	0.1145	0.665	5.791	0.2455
Sept. 14.	18.0	3	18.01	630.4	19.9	5.848	0.1640	0.1163	0.537	5.311	0.2489
	18.0	4	24.72	630.1	22.0	7.791	0.1584	0.0957	0.604	7.187	0.2464
	18.0	4	22.05	630.0	20.6	7.089	0.1612	0.1092	0.650	6.439	0.2469
	18.0	4	21.19	629.8	21.1	6.786	0.1563	0.1066	0.632	6.154	0.2459
	18.0	3	18.74	629.9	20.2	5.997	0.1595	0.1157	0.528	5.469	0.2467
					Air.						
Sept. 15.	18.0	4	21.89	630.7	20.7	6.917	0.1638	0.1088	0.634	6.283	0.2425
	18.0	4	22.29	630.1	21.4	7.018	0.1585	0.1034	0.627	6.391	0.2427
	18.1	3	18.80	628.8	20.2	5.956	0.1641	0.1171	0.539	5.417	0.2440
	18.2	3	19.04	627.4	20.8	5.966	0.1609	0.1150	0.529	5.437	0.2426
	18.2	4	23.96	624.0	21.0	7.472	0.1635	0.1040	0.639	6.833	0.2437
" 19.	18.0	4	22.29	630.2	20.5	7.055	0.1674	0.1130	0.674	6.381	0.2419
					Oxygen (with 9.5 Per Cent. N.).						
Sept. 19.	18.2	3	19.64	634.7	20.1	5.975	0.1677	0.1206	0.553	5.422	0.2315
	18.0	4	23.25	632.9	21.1	7.053	0.1630	0.1094	0.654	6.399	0.2318
	18.0	4	23.65	631.3	21.0	7.109	0.1635	0.1077	0.650	6.459	0.2306
	18.0	3	19.72	633.3	20.8	5.958	0.1604	0.1147	0.527	5.431	0.2317
					Carbon Dioxide.						
Sept. 13.	18.0	3	23.17	630.0	21.8	7.163	0.1573	0.0989	0.483	6.680	0.2443
	18.1	3	23.60	630.0	21.8	7.261	0.1572	0.1000	0.486	6.775	0.2432
	18.0	4	27.67	629.8	22.1	8.472	0.1593	0.0923	0.595	7.877	0.2414
	18.0	4	24.99	629.9	21.7	7.717	0.1578	0.0960	0.604	7.113	0.2412
	18.0	4	20.62	630.0	20.6	6.530	0.1593	0.1096	0.647	5.883	0.2413

Mean Specific Heat between 20° *and* 800°.

1904	t_0	z (Min.).	m (g)	Θ_1	Θ_2	ϑ	τ_1	τ_2	k	ϑ'	c
Nitrogen.											
Aug. 26.	18.0°	4	19.55	804.3°	22.6°	8.310°	0.2201°	0.1551°	0.905°	7.405°	0.2497
	18.0	4	18.72	800.3	22.8	7.988	0.2169	0.1559	0.901	7.087	0.2509
	18.0	4	20.04	799.5	22.4	8.480	0.2178	0.1539	0.897	7.583	0.2509
Sept. 1.	18.0	4	19.63	801.8	22.8	8.319	0.2230	0.1624	0.933	7.386	0.2489
	18.0	4	18.69	800.8	21.8	8.016	0.2247	0.1649	0.944	7.072	0.2503
" 3.	18.0	4	18.77	798.2	22.0	7.944	0.2218	0.1543	0.940	7.004	0.2477
	18.0	4	18.90	797.6	22.4	7.985	0.2199	0.1508	0.892	7.093	0.2495
Air.											
Aug. 16.	20.2	4	19.62	797.7	23.1	8.099	0.2241	0.1630	0.937	7.162	0.2428
	20.0	4	17.79	797.3	23.2	7.380	0.2180	0.1620	0.922	6.458	0.2426
	20.0	4	19.80	793.0	22.7	8.171	0.2244	0.1618	0.934	7.237	0.2436
	20.0	3	15.06	796.8	22.6	6.262	0.2201	0.1691	0.753	5.509	0.2435
" 17.	20.2	3	17.01	798.1	23.4	6.979	0.2203	0.1651	0.743	6.236	0.2439
	20.0	4	18.14	796.3	22.4	7.578	0.2245	0.1672	0.95	6.627	0.2433
	20.0	5	18.96	796.1	23.3	7.973	0.2203	0.1592	1.109	6.864	0.2414
Carbon Dioxide.											
Sept. 1.	17.9	4	20.09	794.0	21.7	8.430	0.2264	0.1613	0.937	7.493	0.2489
	18.0	4	19.62	794.4	22.3	8.212	0.2220	0.1575	0.914	7.298	0.2483
" 3.	18.0	4	19.11	791.6	21.8	8.016	0.2230	0.1556	0.913	7.103	0.2488
	18.0	4	19.29	791.3	22.5	8.018	0.2191	0.1506	0.890	7.128	0.2477
" 5.	18.0	3	19.79	793.5	23.0	8.127	0.2172	0.1505	0.712	7.415	0.2506
	18.1	3	20.97	792.7	22.5	8.568	0.2235	0.1524	0.716	7.852	0.2505
	18.0	4	18.41	791.1	21.9	7.764	0.2230	0.1597	0.957	7.807	0.2477
	18.0	6	20.43	784.3	22.2	8.780	0.2226	0.1545	1.286	7.494	0.2480
	18.0	5	20.32	786.9	22.1	8.563	0.2224	0.1541	1.129	7.434	0.2466

composition of the gas during the experiment by the formation of oxides in the heating tube must be negligible since the passage was so rapid. This was proven by the fact that a specimen of gas sent through rather slowly at 630° showed an increase of less than 1 per cent. of nitrogen. One bomb of nitrogen used contained 1.2 per cent. and the other 5 per cent. oxygen.

RESULTS.

Simple Gases. — The following table shows the mean of the observed values for the mean specific heat of the simple gases.

	Nitrogen.	Oxygen with 9.5 Per Cent. N.	Oxygen.	Air.	Air Calculated from N and O.
Between 20° and 440°	0.2419	0.2255	0.2240	0.2366	0.2377
Between 20° and 630°	0.2464	0.2314	0.2300	0.2429	0.2426
Between 20° and 800°	0.2497	—	—	0.2430	—

The value for pure oxygen was calculated according to the known percentage of nitrogen mixed with it. In the same way a value was calculated for air, derived from the two values for nitrogen and oxygen.

In regard to the specific heat of air between 20° and 440° the difference between our values and those of the earlier observers up to 100° or 200° (Regnault 0.2375, E. Wiedmann 0.2389) lies within the limits of the errors of observation.

Oxygen was investigated by Regnault up to 200°. Two determinations gave for the mean specific heat 0.2163 and 0.2188 giving as an average 0.2175 which is 3.5 per cent. smaller than the value observed by us at 440°. According to this it appears that the specific heat of oxygen increased between 200° and 400°. For comparison we have also made observations on the specific heats of the different gases between 20° and 245°. In this region however, our apparatus was not fitted for absolute measurements. We have therefore merely determined the values relatively, taking air as the normal gas and assuming the Regnault value 0.2375 to be correct.

The results were as follows :

Nitrogen	0.2401
Oxygen with 9.5 per cent. nitrogen	0.2223
Carbon dioxide	0.2197

From this we calculated the value for pure oxygen to be 0.2206 which is still somewhat higher than Regnault found. It is to be observed, however, that these values were derived from observations with comparatively slow gas velocity and very possibly were too small in comparison with the value of air 0.2375 which was found with a powerful gas flow.

So far as we are aware, nitrogen has up to the present never been directly investigated. The value given by Regnault 0.2438 was calculated from his values for air and oxygen.

In regard to the variation of the specific heat with the temperature, it would appear that between 20° and 400°, and 20° and 800° the mean values for nitrogen and air show an increase of 3 per cent. When we consider, however, the variation in the two gases at the same temperature with changes in the condition of the apparatus, and consider further, that the difficulties in determining the temperature of the gas before it enters the calorimeter increase with increasing temperature, it is hardly possible to conclude with certainty from these small changes in the values that the specific heat increases with the temperature. We must therefore at present consider the observed result as merely a limiting value.

Assuming, however, that the variation between 0° and 800° corresponds to the observed values and is linear, and making use of Regnault's values between 10° and 200° we will have the following formula for the mean specific heat c between 0° and θ°

$$c = c_0(1 + 0.00004\theta).$$

where c_0 is the value at 0° and θ the temperature.

Mallard and Le Chatelier as well as Langen have obtained concordant values for the mean specific heat c_v at constant volume at high temperatures by means of explosion experiments. The latter gives for the molecular heat C_v of the simple gases the expression

$$C_v = 4.8 + 0.0006\,\theta$$

for the temperature interval 1300° to 1700°. Assuming that the relation between the molecular heats at constant pressure and constant volume

$$C - C_v = 1.98$$

holds for the whole interval, it follows that the mean specific heat at constant pressure

$$c = c_0 (1 + 0.00008_5 \theta).$$

From our observation it appears that this equation is not applicable to lower temperatures but that here the specific heat increases more slowly.

Carbon Dioxide. — The variation in the specific heat of carbon dioxide is of especial interest, since according to the observations of Regnault and E. Wiedemann there is a well marked increase in its specific heat even at lower temperatures. The following table contains the values of the mean specific heats observed by us. The value for the interval 20° to 200° is taken from earlier observations. In the column Cal. the values given are derived from the formula

$$c = 0.2028 + 0.0000692\theta - 0.0000000167\theta^2.$$

	c	
	Obs.	Cal.
Between 20° and 200°	(0.2168)	0.2173
" 20 " 440	0.2306	0.2312
" 20 " 630	0.2423	0.2410
" 20 " 800	0.2486	0.2486

The true specific heat γ_θ at the temperature θ is

$$\gamma_\theta = 0.2028 + 0.0001384\theta - 0.000000050\theta^2$$

while Regnault from his observations in the interval − 30° to + 210° derived the formula

$$\gamma_\theta = 0.1784 + 0.0002918(\theta + 30^\circ) - 0.0000001074(\theta + 30^\circ)^2.$$

Our investigation therefore shows that the specific heat at higher temperatures increases more slowly than an exterpolation of the Regnault formula would indicate.

We give in the next table the values for the true specific heat as calculated from the different formulæ. It is to be observed that these values on account of their derivation from the integral values at the limits of the observed intervals are to a considerable extent uncertain.

At	Regnault.	E. Wiedemann	Mallard and Le Chatelier.	Langen.	Holborn and Austin.
0°	0.1870	0.1952	0.188_0	0.198_0	0.2028
100	0.2145	0.2169	0.214_0	0.210_0	0.2161
200	0.2396	0.2387	0.239_0	0.222_0	0.2285
400			0.284_0	0.245_0	0.2502
600			0.323_0	0.269_0	0.2678
800			0.355_0	0.292_0	0.2815

The values of Mallard and Le Chatelier correspond to the equation

$$C_v = 6.3 + 0.006\theta - 0.00000118\theta^2.$$

This equation for the mean molecular heat was derived by these investigators from their explosion experiments and from the observations of Regnault and E. Wiedemann. This formula gives considerably larger values than ours which more nearly correspond to Langen's linear equation

$$C_v = 6.7 + 0.0026\theta.$$

If we calculate the mean specific heat at constant pressure between 0° and 1500°, first according to our formula and then according to that of Langen, we get the values 0.269 and 0.287 which differ from each other by 6 per cent.

Since the two ranges of observation lie far apart from each other it will be necessary to postpone definite conclusions until calorimetric measurements are extended to still higher temperatures.

THE QUADRANT ELECTROMETER, AS USED FOR MEASURING CURRENT.

By O. M. Stewart.

THE extensive use of the quadrant electrometer in radio-activity work justifies some mathematical investigation of the properties of this instrument. Since this use is usually limited to the measurement of small currents through some gas, the following discussion is restricted to this particular work.

In measuring current, the needle of the electrometer is usually charged to a relatively high potential, one pair of quadrants is grounded and the other pair is connected to the conductor into which the current from the gas passes. The observer then determines the rate of motion of the electrometer needle and this is taken to be proportional to the current. That is, in ordinary use one assumes that

$$\frac{d\theta}{dt} = k_1 i$$

where θ is the angular deflection of the needle, i the current through the ionized gas and k_1 a constant. The elementary proof of this is sometimes given as follows:

Let C be the capacity of the pair of quadrants and the apparatus connected to it, Q the charge on it and V_1 its potential. Then

$$Q = CV_1. \tag{1}$$

By differentiating, we have

$$\frac{dQ}{dt} = C\frac{dV_1}{dt} = i. \tag{2}$$

If V_2 is the potential of the needle we have

$$\theta = k_2 V_1 V_2, \tag{3}$$

where k_2 is a constant.

Then,

$$\frac{d\theta}{dt} = k_2 V_2 \frac{dV_1}{dt}. \qquad (4)$$

By comparing (2) and (4) one finds that $d\theta/dt$ is proportional to the current i.

This involves two assumptions; first, that the capacity is a constant and second that equation (3) which holds for steady deflections is true when the needle is in motion. Equation (3) follows from a statement of the equilibrium existing between the electrostatic forces which tend to deflect the needle and the torsional force of the suspension which tends to restore the needle to its zero. This equation is not true when the needle is in motion, for in that case there is another force introduced, the damping. Even for a uniformly increasing potential and a uniform velocity of the needle, equation (3) does not hold, for due to this force of damping which tends to assist the torsional force of the suspension, the deflection is always less than for the steady deflection.

The capacity of the electrometer changes as the needle moves; but if the capacity of the apparatus connected to the electrometer is large this change may be neglected. However, in many instances this cannot be neglected. Professor Thomson[1] has shown that when a needle moves there is a certain effective capacity which for a given potential of the needle is a constant. He has, however, assumed equation (3) which as we have just seen is not correct when θ is varying. But this equation has been used in such a way that as will be shown later his results are correct when the velocity of the needle has become constant. That is, the effective capacity is a constant when the needle is moving without acceleration. This will be discussed more in detail later. For the present we will assume that the capacity is constant, that is, the special case where the capacity of the apparatus is large compared to that of the electrometer.

If we assume a constant capacity and wish to measure a steady current i we have, from (2),

$$i = C\frac{dV_1}{dt},$$

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[1] Philosophical Magazine, 46, p. 537, 1898.

and by integration

$$V_1 = \frac{i}{C}t,$$

where V_1 is the varying potential of one pair of quadrants. The moment of force tending to deflect the needle is at any instant equal to

$$kV_1V_2,$$

when the potential of the needle, V_2, is large compared to V_1. Hence the moment of force is given by

$$\frac{ki}{C}V_2t = Et. \tag{5}$$

Since the factors of the coefficient of t are here assumed constant E is a constant. E may be said to be the time rate of change of the electrostatic torque on the needle.

The general equation of the motion of the needle may then be written,

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D\theta = Et, \tag{6}$$

where A is the moment of inertia of the needle, B the damping factor and D is the moment of torsion of the fiber.

The complementary solution of this equation is obtained by equating the left hand member to zero and solving.

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D\theta = 0. \tag{7}$$

The solution of (7) is

$$\theta = Me^{(\alpha+\gamma)t} + Ne^{(\alpha-\gamma)t}, \tag{8}$$

where

$$\alpha = -\frac{B}{2A}$$

and

$$\gamma = \sqrt{\frac{B^2}{4A^2} - \frac{D}{A}}.$$

The particular solution of (6) is

$$\theta = \frac{E}{D}\left(t - \frac{B}{D}\right). \tag{9}$$

Hence the complete solution is

$$\theta = Me^{(\alpha+\gamma)t} + Ne^{(\alpha-\gamma)t} + \frac{E}{D}\left(t - \frac{B}{D}\right). \tag{10}$$

In this solution, γ may be real or imaginary. Equation (10) will therefore reduce to one of two types, depending on the relation between the damping on the one hand and the moments of inertia and torsion on the other. There is also the special case where $\gamma = 0$.

γ real.

In this case

$$B^2 > 4\,AD.$$

When the time t is zero we know that

$$\theta = 0, \text{ and } \frac{d\theta}{dt} = 0.$$

Applying these initial conditions to equation (10) and solving for the constants M and N, one obtains

$$M = -\frac{E}{2D\gamma}\left(1 + (\alpha - \gamma)\frac{B}{D}\right),$$

$$N = \frac{E}{2D\gamma}\left(1 + (\alpha + \gamma)\frac{B}{D}\right).$$

Substituting these in (10),

$$\theta = \frac{E}{D}\left\{\frac{1}{2\gamma}e^{(\alpha-\gamma)t}\left(1 + (\alpha + \gamma)\frac{B}{D}\right)\right.$$
$$\left. - \frac{1}{2\gamma}e^{(\alpha+\gamma)t}\left(1 + (\alpha - \gamma)\frac{B}{D}\right) + t - \frac{B}{D}\right\} \tag{11}$$

From this by differentiating and remembering that $\alpha = -B/2A$ and that $\alpha^2 - \gamma^2 = D/A$, the value of the angular velocity is

$$\frac{d\theta}{dt}=\frac{E}{D}\left(1-\frac{\kappa+\gamma}{2\gamma}e^{-(\kappa-\gamma)t}+\frac{\kappa-\gamma}{2\gamma}e^{-(\kappa+\gamma)t}\right). \tag{12}$$

For convenience κ has been written for $-\alpha$. When t is large

$$\frac{d\theta}{dt}=\frac{E}{D}$$

Hence the angular velocity approaches a constant value which depends only on E and D the moment of torsion.

γ zero.

Equation (10) is not a complete solution of (6) when γ is zero for it then contains only one constant. The form of the solution of (7) may be taken as

$$\theta=e^{\alpha t}(R+St)$$

and the complete solution of (6) as

$$\theta=e^{-\frac{B}{2A}t}(R+st)+\frac{E}{D}\left(t-\frac{B}{D}\right).$$

Putting in the initial conditions one has for the displacement,

$$\theta=e^{-\frac{B}{2A}t}\left(\frac{BE}{D^2}+\frac{E}{D}t\right)+\frac{E}{D}\left(t-\frac{B}{D}\right)$$

or

$$\theta=\frac{E}{D}\left[e^{-\frac{B}{2A}t}\left(\frac{B}{D}+t\right)+t-\frac{B}{D}\right]. \tag{13}$$

The angular velocity becomes on differentiating

$$\frac{d\theta}{dt}=\frac{E}{D}\left[1-e^{-\frac{B}{2A}t}\left(1+\frac{B}{2A}t\right)\right],$$

since $B^2=4AD$ when $\gamma=0$.

Writing κ for $B/2A$ this becomes,

$$\frac{d\theta}{dt}=\frac{E}{D}\left[1-e^{-\kappa t}(1+\kappa t)\right]. \tag{14}$$

In this case also the angular velocity $d\theta/dt$ becomes practically equal to E/D after some time.

γ imaginary.

Let $\gamma = i\beta$ where $i = \sqrt{-1}$
Then

$$\beta^2 = \frac{D}{A} - \frac{B^2}{4A^2}.$$

The solution of equation (7) is now

$$\theta = e^{\alpha t}(M' \cos \beta t + N' \sin \beta t)$$

and the complete solution of (6) is

$$\theta = e^{\alpha t}(M' \cos \beta t + N' \sin \beta t) + \frac{E}{D}\left(t - \frac{B}{D}\right). \tag{15}$$

Applying the initial conditions

$$\theta = 0 \text{ and } \frac{d\theta}{dt} = 0,$$

and substituting the values of M' and thus N' obtained in (15) we have

$$\theta = \frac{E}{D}\left[\frac{B}{D}e^{\alpha t} \cos \beta t - \frac{1}{\beta}\left(\frac{\alpha B}{D} + 1\right)e^{\alpha t} \sin \beta t + t - \frac{B}{D}\right]. \tag{16}$$

Differentiating this and remembering that $\alpha^2 + \beta^2 = D/A$, the expression for the angular velocity is obtained

$$\frac{d\theta}{dt} = \frac{E}{D}\left[1 - e^{-\kappa t}\left(\cos \beta t + \frac{\kappa}{\beta} \sin \beta t\right)\right], \tag{17}$$

as before κ has been written for $-\alpha$.

In this case the velocity approaches the final velocity E/D with a damped periodic motion. The period of this motion is given by

$$\tau = \frac{2\pi}{\beta}.$$

By solving (17) for maximum and minimum values of the velocity, it may be shown that the velocity reaches a maximum at $t = \tau/2$, a minimum at $t = \tau$, with another maximum at $t = 3\tau/2$ and so on.

The velocities at these times are given by the following equations: When,

$$t = \frac{\tau}{2}, \qquad \frac{d\theta}{dt} = \frac{E}{D}\left(1 + e^{\frac{-\kappa\tau}{2}}\right),$$

$$t = \tau, \qquad \frac{d\theta}{dt} = \frac{E}{D}\left(1 - e^{-\kappa\tau}\right),$$

$$t = \frac{3}{2}\tau \qquad \frac{d\theta}{dt} = \frac{E}{D}\left(1 - e^{\frac{-3\kappa\tau}{2}}\right),$$

In curve 1, on p. 238, is shown the relation between the angular velocity and the time. The data for this curve was obtained from equation (17) by substituting in it the constants of a particular instrument. The angular velocities are plotted relatively, the final velocity E/D being taken as unity.

Hence in all cases as is shown by equations (12), (14) and (17), the final velocity is given by

$$\frac{d\theta}{dt} = \frac{E}{D}.$$

That is, the final velocity depends only on E, the rate of change of the electro-static torque acting on the needle and D the moment of torsion of the suspension.

Substituting the value of E from equation (5) in the above value of $d\theta/dt$ we have

$$\frac{d\theta}{dt} = \frac{kiV_2}{CD}. \tag{18}$$

But kV_2/D is the constant k' of the electrometer in the equation

$$\theta = k'V_1.$$

The final uniform velocity is therefore proportional to the current whose value is sought. If the capacity C is known, then i can be at once determined. It may be noted that the final velocity is independent of the moment of inertia of the needle and B the damping coefficient.

The important question that arises in every case is, — How long is it until the needle reaches this final velocity? Considerable light may be thrown on this by considering another motion of the needle. Let the free pair of quadrants be raised to any convenient potential and the steady deflection θ_0 noted. If the quadrants are now grounded, the needle will return to its zero position. The equation of its motion in this case is given by

$$A\frac{d^2\theta}{dt} + B\frac{d\theta}{dt} + D\theta = 0.$$

The complete solution of this is

$$\theta = Me^{(\alpha+\gamma)t} + Ne^{(\alpha-\gamma)t}, \tag{19}$$

where as before, $\alpha = -B/2A$ and $\gamma^2 = B^2/4A^2 - D/A$. As before three cases arise, γ real, imaginary, and equal to zero. In each case we have the initial conditions,

$$\theta = \theta_0, \quad \frac{d\theta}{dt} = 0.$$

When γ is real, equation (19) becomes, on substituting for M and N the values found by these initial conditions,

$$\theta = \theta_0\left(\frac{\kappa+\gamma}{2\gamma}e^{-(\kappa+\gamma)t} - \frac{\kappa-\gamma}{2\gamma}e^{-(\kappa+\gamma)t)}\right), \tag{20}$$

or the motion is aperiodic. As before κ has been written for $-\alpha$. When γ is imaginary (19) becomes

$$\theta = e^{-\kappa t}(M\cos\beta t + N\sin\beta t). \tag{21}$$

Solving again for M and N by applying the initial conditions and inserting these values in (21) one obtains

$$\theta = \theta_0 e^{-\kappa t}\left(\cos\beta t + \frac{\kappa}{\beta}\sin\beta t\right). \tag{22}$$

In this case the needle swings through the zero and the period of its vibration is given by

$$\tau = \frac{2\pi}{\beta}.$$

Proceeding in a similar way for the case $\gamma = 0$ one obtains

$$\theta = \theta_0 e^{-\kappa t}(1 + \kappa). \tag{23}$$

In the equations (20), (22) and (23) the quantities κ, γ and β are the same as before.

The terms that contain the coefficients of the exponentials in equations (12), (14), (17) are identical with the corresponding terms in equations (20), (23) and (21). Hence we find a general rule *that the velocity approaches its final value at the same rate and in the same manner that the deflected needle when released by grounding the quadrants, returns to its zero.* For example, suppose that the needle of a particular instrument had been displaced a scale distance of 20 cm. and then released. It was noted that 25 seconds elapsed before the needle was within 1 cm. of its zero, or 5 per cent. of the initial deflection. Then if this instrument were used to measure a constant current, it would be 25 seconds from the time of insulating the quadrants until the velocity of the needle had come within 95 per cent. of the final value.

The maximum values of θ in (22) occur when, $t = 0$, $t = \tau$, $t = 2\tau$, etc. Or when

$$\begin{aligned} t &= 0, & \theta_1 &= \theta_0, \\ t &= \tau, & \theta_2 &= \theta_0 e^{-\kappa\tau}, \\ t &= 2\tau, & \theta_3 &= \theta_0 e^{-2\kappa\tau}. \end{aligned}$$

From this it is seen that,

$$\log_e \frac{\theta_1}{\theta_2} = \kappa\tau.$$

Or $\kappa\tau$ is the "logarithmic decrement." Since τ can be observed, κ may be computed. Thus, from the observations on the decay of a vibration the constants, κ and β, of the equation (17) can be computed. In this way the period and logarithmic decrement of a sensitive electrometer of the Dolezalek type[1] were observed. Curve I. shown in the figure was plotted by substituting these values in equation (17). In this instrument only air damping is used. As is shown by this curve it is necessary to wait about 30 seconds before the velocity becomes approximately constant. It is of some practical interest to know what can be gained by changing the constants of the instrument to shorten this time. With this electrometer observation gave

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[1] Made by Cambridge Instrument Co.

$$\tau = 24 \text{ seconds}$$

and the mean ratio of consecutive throws 22.6. Hence

$$\log_e 22.6 = 3.12 = \kappa\tau.$$

Or

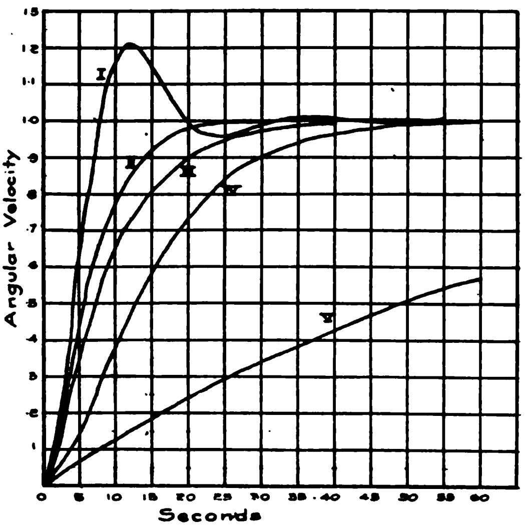
$$\kappa = .13.$$

But since,

$$\frac{D}{A} - \kappa^2 = \beta^2 = \frac{4\pi^2}{\tau^2} = .68,$$

$$\frac{D}{A} = .085.$$

If κ^2 be increased to .085, that is if κ be increased from 0.13 to 0.29 β becomes zero and the motion aperiodic. Curve II. was computed from equation (14) by using this changed value of κ. It is seen from this curve that there is a distinct gain in increasing the damping.



If the damping be increased beyond this critical value, the velocity will approach its final constant value more slowly. Curve III. is the result obtained when the damping factor is increased about 35 per cent. of the value used in the case of Curve II., all the other quantities remaining unchanged. Curve V. shows the effect of increasing the damping ten fold. Both of these curves are computed from equation (12). It is apparent that too much damping is to be avoided. In adjusting the damping, use can be made of the rule just given, that is by noting how soon the needle returns to zero after being deflected.

If instead of changing the damping a more delicate fiber be used the motion may become aperiodic, for D is decreased and D/A may become less than κ^2. However the undamped period is increased and in general the time for the velocity to reach an approximately constant value is not decreased. Curve IV. was plotted from equation (14) by assuming that D had been decreased until the motion just became aperiodic. D would have to be reduced to one fifth its original value. While there has been in this way a decided gain in sensibility, a considerably longer time is required for the needle to reach a uniform speed.

Capacity not Constant.

In the preceding work it has been assumed that the capacity of the electrometer as compared to that of the rest of the apparatus was so small that the change in it could be neglected. We shall now consider the more general case, that where the change in the capacity of the quadrants is taken into account.

If V_1 is the potential of one pair of quadrants, V_3 that of the other and V_2 that of the needle we have, Q_1 being the charge on the first pair of quadrants,

$$Q_1 = q_{11}V_1 + q_{12}V_2 + q_{13}V_3, \tag{24}$$

where q_{11}, q_{12}, q_{13} are coefficients of capacity. q_{11} is the charge on 1 when V_1 is unity and all others are grounded; q_{12} is the charge on 1 when V_2 is unity and all others are grounded, and so for q_{13}. We shall consider that one pair of quadrants is always grounded, that is that $V_3 = 0$. When the needle moves both q_{11} and q_{12} change. If the needle is approximately symmetrically placed with respect to the quadrants and θ is not large, one may assume the change in q_{12} is proportional to the deflection, or that

$$\frac{dq_{12}}{d\theta} = a,$$

a constant. With this assumption it has been shown,[1] that

$$q_{12} = C_{12} + a\theta,$$

$$q_{11} = C_{11} - a\theta,$$

where C_{12} and C_{11} are the values of q_{12} and q_{11} when θ is zero. Substituting these values in equation (24) and remembering that V_3 is always zero, we have

$$Q_1 = C_{11}V_1 + C_{12}V_2 + a\theta(V_2 - V_1) \tag{25}$$

The potential of the needle, V_2, is large compared to V_1, hence we may neglect V_1 in the last term. Solving (25) for V_1,

$$V_1 = \frac{1}{C_{11}}(Q_1 - C_{12}V_2 - a\theta V_2). \tag{26}$$

But the electrostatic moment of force tending to deflect the needle is

$$kV_1V_2.$$

Substituting in this the above values of V_1 we have for the value of the moment,

$$\frac{kV_2}{C_1}(Q_1 - C_{12}V_2 - a\theta V_2). \tag{27}$$

$C_{12}V_2$ is quantity of electricity induced on the quadrants when V_1 and θ are zero, and the increase due to a current i is

$$Q_1 - C_{12}V_2 = it.$$

Substituting this we have for the deflecting moment

$$\frac{kV_2}{C_{11}}(it - a\theta V_2). \tag{28}$$

The equation of motion then becomes

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D\theta = \frac{kV_2}{C_{11}}(it - a\theta V_2),$$

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[1] Maxwell, "Electricity and Magnetism," Vol. I., Art. 219; Thomson, Phil. Mag., 46, p. 537, 1898.

or

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + \left(D + \frac{akV_2^2}{C_{11}}\right)\theta = \frac{kV_2 i}{C_{11}}t. \tag{29}$$

This may be written

$$A\frac{d^2\theta}{dt^2} + B\frac{d\theta}{dt} + D'\theta = Et. \tag{30}$$

The coefficient of θ is the only quantity in this equation that differs from equation (6). Hence it appears that the effect of this increase of capacity is mechanically the same as an increase in the moment of torsion of the suspension. There is this difference that while the change in the capacity is continuous, the equivalent change in the moment of torsion is an absolute change. The capacity C_{11} includes the capacity of the apparatus connected to the free quadrants

The value of the velocity obtained from (30) is

$$\frac{d\theta}{dt} = \frac{E}{D'}\left[1 - e^{-\kappa t}\left(\cos\beta' t + \frac{\kappa}{\beta'}\sin\beta' t\right)\right], \tag{31}$$

where

$$\beta' = \frac{D'}{A} - \frac{B^2}{4A^2}.$$

As D' is larger than D, β' is larger than β and the periodic time is shortened. Since κ is not changed and the period less, the needle will reach the approximately uniform velocity sooner.

The solution in the aperiodic case is

$$\frac{d\theta}{dt} = \frac{E}{D'}\left[1 - \frac{\kappa + \gamma'}{2\gamma'}e^{-(\kappa - \gamma')t} + \frac{\kappa - \gamma'}{2\gamma'}e^{-(\kappa + \gamma')t}\right], \tag{32}$$

where

$$\gamma'^2 = \frac{B^2}{4A^2} - \frac{D'}{A}.$$

Owing to the increase of D', γ' is less than γ. The second term on the right hand side of (32) is larger than the last and is therefore, so far as the decay is concerned, the more important term. This term is decreased by the decrease in γ. Hence the time for the velocity to reach an approximately uniform velocity is shortened. This increase in D tends to make an aperiodic motion become periodic, but even in this case will not tend to increase the time for the acquirement of a practically uniform velocity.

When the velocity becomes uniform, in each case,

$$\frac{d\theta}{dt}=\frac{E}{D'}=\frac{kiV_2}{D\left(C_{11}+\frac{k}{D}aV_2^2\right)}. \tag{33}$$

Here, as in the case where the capacity was regarded as a constant, the velocity is proportioned to the current. In the case where the capacity was uniform it was shown that the simple method of noting the time for the needle to return to approximate rest at its zero point gives the time for the velocity to become approximately constant. When the change of capacity is appreciable, this time is shortened. This method, however, gives a safe limit for the beginning of observations.

On comparing equation (33) to equation (18) it is seen that the quantity

$$C_{11}+\frac{k}{D}aV^2$$

corresponds to the capacity C in that equation. It has been called the effective capacity and the value as here found is identical to that found by Professor Thomson. This quantity, however, is the effective capacity only when the velocity of the needle has become uniform.[1] It is this capacity that one measures when the divided charge method is employed and the change in the deflection of the electrometer itself is used.[2]

If k' be defined by the equation

$$\theta=k'V_1V_2,$$

where θ is the steady deflection,

$$k'=\frac{k}{D}.$$

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[1] Strictly speaking, it is the effective capacity when there is no acceleration. It is the effective capacity when the needle is moving with uniform speed and also when the needle is allowed to come to rest as in the method of measuring charges or capacities.

[2] For example, the method given in Rutherford's "Radioactivity," p. 86.

The effective capacity[1] may then be written

$$C_{11} + k'aV_2^2.$$

An inspection of equation (33) shows that as the potential of the needle is increased the velocity $d\theta/dt$ goes through a maximum value. This maximum value is reached, as shown by differentiating (33) and equating to zero, when

$$C_{11} = \frac{k}{D}aV_2^2 = k'aV_2^2. \tag{34}$$

The maximum sensibility for current work as the potential of the needle is increased, is therefore reached when the effective capacity is twice the capacity in the case where the needle is kept at zero This however assumes that k' is constant. It is well known that k changes when the potential of the needle becomes large, so that the sensibility as indicated by steady deflections passes a maximum as V_2 is increased. If however the capacity of the apparatus connected to the electrometer is small, it may happen that the potential of the needle is above the maximum value of current sensibility yet well within the maximum for ordinary sensibility. The sensibility for current measurement however does not change much with the change of the potential of the needle, so that there is no practical gain in adjusting the needle potential to this maximum.

Equation (33) may be written

$$\frac{d\theta}{dt} = \frac{kiV_2}{DC_{11} + kaV_2^2}.$$

The only quantity in this equation affected by changing the suspension is D the moment of torsion of the suspension. It is obvious that while the sensibility of the electrometer for a steady deflection is inversely proportional to D, the sensibility for current measurements is not effected as much by changes in D.

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[1] It may be shown, see Maxwell, l. c., that

$$a = k,$$

hence the effective capacity may be written

$$C_{11} + k'kV^2.$$

The ratio between the change of the capacity of the electrometer due to the motion of the needle and the capacity when the needle is stationary can be found experimentally by a simple method. Starting with the quadrants earthed, one pair is insulated and then connected for an instant only to some source having a potential V_1. If this pair has been insulated before the needle moves an appreciable amount, the needle will swing around to a deflection θ_1. If however connection to the potential V_1 is maintained until the needle comes to rest, a deflection θ_2 is observed. The ratio of this last deflection to the other is the ratio of the effective capacity to the capacity when the needle does not move. Another method is to let the needle take a deflection θ corresponding to the potential V of the free quadrant. This pair of quadrants is now insulated and then grounded for an instant. The needle will not return to zero but will take a deflection θ_1. The ratio of the deflection θ to θ_1 is equal to the ratio of the effective capacity to the difference between the effective capacity and that when the needle is not free to move. Both of these statements are readily proven. If the potential of the other pair of quadrants is always zero and the needle is charged to a potential high compared to that used on the quadrants, equation (25) may be written

$$Q_1 = C_{11}V_1 + C_{12}V_2 + a\theta V_2.$$

If in the first case θ be zero and a potential V_1 be applied we have

$$Q_1 = C_{11}V_1 + C_{12}V_2.$$

When the needle moves Q_1 remains constant and V_1 changes to V'. The needle will come to rest at θ_1 and

$$Q_1 = C_{11}V' + C_{12}V_2 + a\theta_1 V_2$$

where θ_1 is the deflection corresponding to a potential V'.

Equating the two left handed members we have

$$C_{11}V_1 = C_{11}V' + a\theta_1 V_2.$$

But

$$\theta_1 = k'V'V_2,$$

$$\therefore C_{11}V_1 = (C_{11} + k'V_2^2)V',$$

$$\therefore \frac{V_1}{V'} = \frac{C_{11} + ak'V_2^2}{C_{11}} = \frac{\theta_2}{\theta_1}.$$

Or

$$\frac{ak'V_2^2}{C_{11}} = \frac{\theta_2}{\theta_1} - 1.$$

It may be shown in a similar manner that in the second case

$$\frac{C_{11} + ak'V_2^2}{ak'V_2^2} = \frac{\theta}{\theta_1},$$

or

$$\frac{C_{11}}{k'V_2^2} = \frac{\theta}{\theta_1} - 1.$$

These methods assume that the period of the needle is large enough so that a contact can be made and broken before the needle moves an appreciable amount. If large deflections are used, errors due to the small charge given by contact effects at the make and break point are not important. Moreover, if the same metal is used for both surfaces of the contact key, as for example, two clean pieces of copper wire, the disturbing effect will be insignificant.

A trial with the electrometer, from which curves shown in Fig. 1 were deduced, gave by both methods the ratio

$$\frac{ak'V_2^2}{C_{11}} = 2.0.$$

V_2 was in this case about 100 volts. With this potential of the needle the electrometer gave about 600 mm. deflection on a scale 1 meter distant for a difference of potential of one volt.

By using one of these methods with and without the rest of the apparatus connected to the electrometer one can compare the capacity of the whole to that of the electrometer itself.

There is a method available for comparing currents in which one does not need to wait until the velocity has become uniform. The method is to observe the deflection reached in a given time after the quadrants are insulated. If the same time interval is used in all the observations, the deflection in each case will be proportional to the current. This can be seen by an inspection of the equations (11), (13) and (16). Since A, B and D, and therefore α, β and γ are constants, θ is proportional to E if a constant value of t is used. But E, see equation (5), is proportional to the current i. This is also true in the general case where the capacity is not a constant. For in this case the effect is to change D to D', see equation (30), and D' is a constant. This method is of great advantage where the readings must be taken quickly. It has the disadvantage that with sensitive electrometers the break of the earth connection often imparts a slight initial charge to the quadrants. The equations (11) (13) and (16) show that the deflection for a given value of t is not proportional to the sensibility of the instrument. For example the sensibility varies inversely with D, yet this deflection according to these equations will not vary inversely as D. This method has the additional disadvantage, that the absolute value of the current can not readily be computed, as in the case where one waits until the velocity has become uniform.

The method of comparing or determining the current by observing the time required for the needle to move a certain amount does not give correct results unless the needle is moving with a uniform velocity.

STUDIES OF LUMINESCENCE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

V. THE LUMINESCENCE OF SIDOT BLENDE.[1]

AMONG the substances whose luminescence is sufficiently bright for spectrophotometric study Sidot blende, or phosphorescent zinc sulphide, seems especially well suited to bring out the relationships that doubtless exist between different types of luminescence; for not only is this substance excited to luminescence by all known exciting agents — light, Roentgen rays, radium rays, cathode rays, etc. — but the stimulating effect of heat, and the property possessed by the red and infra-red rays of suppressing phosphorescence, are exhibited in unusual degree. It is for this reason that we have chosen this substance for spectrophotometric study. While it is our intention to extend this study to all of the various types of luminescence whose quantitative investigation is practicable, the present communication deals only with luminescence excited by light and by Roentgen rays.

The material used in these experiments was in the form of a screen, of the kind frequently used in exhibiting the properties of radium and for numerous experiments in which it is desirable to have a fluorescent substance in convenient form. The experimental methods were similar to those employed in our previous work on fluorescence, a Lummer-Brodhun spectrophotometer, with an acetylene flame as a comparison source, being used to measure the intensity in different parts of the luminescence spectrum. In certain portions of the work special devices were required which will be described in their proper place.

LUMINESCENCE EXCITED BY ROENTGEN RAYS.

The screen was placed in front of the collimator slit of the spectrophotometer at a distance of only a few centimeters, while the

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[1] An account of the experiments described in this paper was presented to the American Physical Society at the Philadelphia meeting December 30, 1904. An abstract appeared in the PHYSICAL REVIEW vol. 20, p. 120, 1905.

Queen self regulating tube used for excitation was about twenty centimeters behind the screen. Roentgen rays of moderate "hardness" were used. No systematic experiments to determine the effect of varying hardness upon the form of the luminescence spectrum have yet been made, but a few preliminary tests indicate that the effect is not great. Corrections due to fluorescence excited in the glass of the spectrophotometer, which we had at first thought would be necessary, were found to be negligible.

The upper curve in Fig. 30 shows the luminescence spectrum observed during excitation, while the lower curve shows the distribution of intensity in the phosphorescence spectrum, observed 5 sec. after excitation had ceased. Owing to the weakness of the phosphorescence excited by Roentgen rays, the latter curve was determined with some difficulty, the readings at the red end of the spectrum being especially uncertain. The indications of a second maximum in the phosphorescence spectrum at 0.62 μ or beyond are therefore not to be regarded as entirely trustworthy.

PHOTO-LUMINESCENCE DURING EXCITATION.

In the experiments upon photo-luminescence during excitation the carbon arc was first used as an exciting source. The arrangement of apparatus is shown in Fig. 31. The zinc sulphide screen was placed in a light tight box B, and the exciting light from an arc A, after dispersion by the pris m P, entered the box through an open

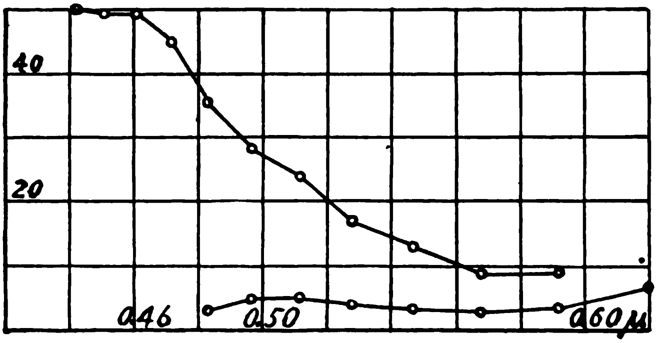

Fig. 30. The upper curve shows the luminescence spectrum of Sidot blende during excitation by Roentgen rays. The lower curve shows the phosphorescence 5 seconds after excitation.

ing at the left. A second opening in *B* allowed the fluorescence light to enter the slit of the Lummer-Brodhun spectrophotometer S_1. The comparison source was an acetylene flame *F* whose rays were reflected into the comparison slit by the block of magnesium carbonate, *M*. The second spectrophotometer, S_2, and the shutter *C* were used in later experiments on phosphorescence, but not in the experiments now considered.

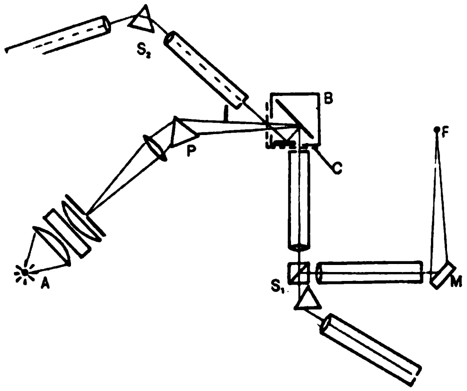

Fig. 31.

Luminescence was excited only by the rays at the violet end of the arc spectrum, and especially in the region of the violet bands. It is to be noted that on account of the absorption of the glass prism and lenses the spectrum extended only a short distance into the ultra violet.

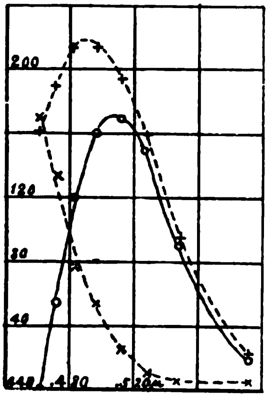

Fig. 32. Luminescence spectrum of Sidot blende during excitation by the violet bands in the arc.

Observations taken to determine the luminescence spectrum when the zinc sulphide screen was excited by the violet bands of the arc are plotted in Fig. 32. Owing to the impurity of the exciting spectrum a certain amount of blue and green light reached the screen even when the attempt was made to excite by violet only. Since this stray light was in part reflected into the slit of the spectrophometer with the luminescence light of the same color, it was necessary to make a correction to remove the error due to this cause. The correction was determined by replacing the zinc sulphide screen by a block of magnesium carbonate, whose surface was of approximately the same color and roughness as that of the fluorescent screen, and by measuring the light received from the magnesia at different points throughout the spectrum. The results of such a series of measurements is shown in the lower broken line in the figure. It will be noticed that the correction is inappreciable for the longer wave-lengths, but becomes important in the violet. The upper broken line in Fig. 32 shows the intensity of the light reaching the spectrophotometer from the zinc sulphide screen, being the combined effect of luminescence and reflected light; and the heavy curve, obtained by subtracting the ordinates of the lower curve from those of the upper, shows the corrected luminescence spectrum during excitation.

The curves in Fig. 32, like those published in our previous papers on luminescence, are expressed in terms of the acetylene flame as a standard. In other words, each ordinate represents the ratio of the intensity of the luminescence light, of the particular wave-length considered, to the intensity of the light of the same wave-length from an acetylene flame; the curves are not energy curves. Since, however, the distribution of energy in the visible spectrum of the acetylene flame is now known,[1] curves showing the energy distribution in luminescence spectra may readily be computed if desired.

When the screen was excited by the arc as described above no trace of the violet luminescence, which had been so prominent with Roentgen ray excitation, could be observed. It seemed not unlikely, however, that the absence of the violet band was due to the fact that the ultraviolet rays suitable for exciting it had been removed from the light from the arc by the glass prism and lenses of the dispersing system. We therefore rearranged the apparatus so as to use a quartz prism and quartz lenses, while a spark between metal terminals was substituted for the arc. Since the excitation in the region studied was solely by ultraviolet rays that were incapable of passing through glass, it was a simple matter to test for errors due an impure spectrum, or to any other source of stray light, by inserting a piece of glass in the path of the exciting rays. This test showed that stray light was in no case present in appreciable amount.

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[1] Nichols, Standards of Light, Proc. International Electrical Congress at St. Louis, 1904. Physical Review, vol. XXI., p. 147, 1905.

This ultraviolet excitation developed strong fluorescence in the extreme violet, similar in color to that produced by Roentgen rays. But the green band that had been excited by the visible rays of the arc was relatively very weak. In spite of its faintness, however, the presence of the green band in the luminescence light could be readily detected, for while the violet luminescence died out almost immediately when excitation ceased, the green persisted as a slowly decaying phosphorescence observable for several minutes.

The similarity between the effects of ultraviolet light and those of Roentgen rays as exciting sources is worthy of note. In each case the chief luminescence is in the extreme violet, and is of short duration. But in each case also this is accompanied by luminescence in the green, which is relatively faint but of long duration. As is illustrated in numerous other cases, the Roentgen rays, when comparable at all with rays of light, are rather to be compared with ultraviolet light than with the rays of the visible spectrum.

The agreement between the luminescence spectrum excited by Roentgen rays and that observed in the case of ultraviolet excitation is not exact. We are of the opinion that the difference is due to the fact that the violet luminescence does not consist of one band only, but of at least two, which are excited by Roentgen rays and

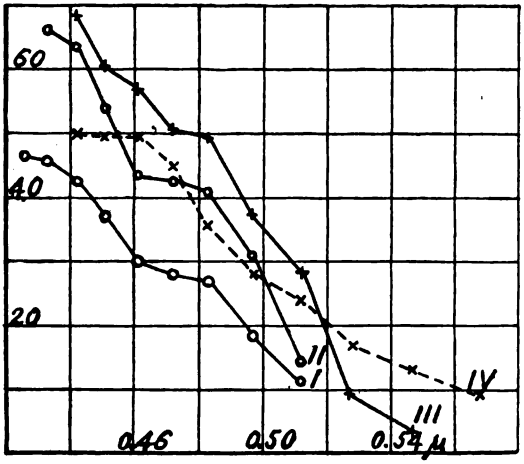

Fig. 33. Fluorescence spectrum of Sidot blende when excited by the ultra-violet rays of the iron spark (Curves I. and II.), by the ultra-violet of the magnesium spark (Curve III.), and by the Roentgen Rays (Curve IV.).

ultraviolet light in different relative intensity. The matter will be made clear by reference to Fig. 33. Curve I. shows the luminescence spectrum when ultraviolet rays from the iron spark were used for excitation. The rays used were those giving most intense luminescence, and did not lie much beyond the edge of the visible spectrum. The shape of this curve suggests that it is made up of two overlapping bands, one having a maximum not far from 0.48 μ, while the other has its maximum near 0.42 μ. In Curve II. the exciting light was at the extreme ultra end of the iron spectrum, and in Curve III. the magnesium lines near 0.33 μ were used in excitation. In these curves also there is every indication that the spectrum consists of at least two bands.

Unfortunately we have not been able to separate the bands more completely. It is to be remembered that the resolving power of a spectrophotometer is at the best small, and that in experiments of the kind here described the small intensity of the light studied prohibits the use of a narrow slit. Luminescence bands may sometimes be separated by a proper choice of the exciting light. In the case of Sidot blende the green band is very readily obtained alone by using the carbon bands of the arc for excitation. But the two violet bands in the luminescence of this substance are so close together that their regions of excitation appear to overlap throughout nearly their whole extent. The most that we were able to do was to show that ultraviolet rays of different wave-length produced different relative intensities in the two bands, as illustrated by Curves I. and III. of Fig. 33.

The broken line, Curve IV. of Fig. 33 shows the luminescence spectrum excited by Roentgen rays. This is the same curve that appears in Fig. 30, and is introduced in Fig. 33 to make possible convenient comparison of the effects of ultraviolet light and Roentgen rays. It will be observed that each of the curves in Fig. 33 might well result from the superposition of three bands, whose maxima lie approximately at 0.42 μ, 0.48 μ and 0.51 μ. In the Roentgen ray luminescence the green band is relatively stronger than in the case of excitation by ultra-violet light, while the band at 0.48 μ appears to be entirely absent. In the luminescence produced by the magnesium spark (Curve III.) the green band, while still observable, is not so strong as in Curve IV., while the band at 0.48 μ is readily detected. Curves I. and II. (iron spark) show scarcely any trace of the green band, but the bands at 0.48 μ and at 0.42 μ are well marked.

FAILURE OF STOKES' LAW.

As already stated, the green band is most brilliantly excited by the violet, although rays from all parts of the ultraviolet spectrum are also capable of producing a considerable effect. We thus see that there is the same general relation between the position of the luminescence spectrum and that of the exciting light as in the case of fluorescence. In all the cases of fluorescence thus far studied we have found that the two spectral regions overlap. It therefore seemed interesting to see whether the same is true in the present case.

To settle this point it was necessary to use in excitation a far purer spectrum than that employed in our other experiments with Sidot blende. The rather crude dispersing system shown in Fig. 31 was therefore replaced by a large spectrometer. A spectrum of the arc was thrown on the collimator slit by the aid of a prism and single lens, and after a second dispersion in the spectrometer, light reached the phosphorescent screen as a sharply focussed band. Using the shutter described below so as to observe the phosphorescence immediately after the exciting light was cut off, and making observations with the unaided eye instead of with the spectrophotometer, it was found that phosphorescence was unquestionably present for exciting light lying between 0.470 μ and 0.497 μ. Since the phosphorescence spectrum can readily be followed beyond 0.46 μ there appears to be the same violation of Stokes' law in the phosphorescence of Sidot blende that we have previously found in the case of fluorescence.

PHOSPHORESCENCE SPECTRUM DURING DECADENCE.

Although the phosphorescence of Sidot blende can be detected in a dark room for several hours after excitation has ceased, it remains sufficiently bright for spectrophotometric measurement only for a few seconds. In order to determine the law of decay for different wave-lengths and especially to determine the change, if any, in the phosphorescence spectrum during decay, the following procedure was followed:

A shutter, shown by the broken line *C* in Fig. 31, and sliding upon vertical guides, was attached to the box containing the phosphorescent screen. When this shutter was raised it permitted the exciting light to enter the box, as in the experiments just described, but at the same time closed the opening in front of the collimator slit. When the shutter was dropped it first cut off the exciting light and then, a moment later, opened the window in front of the collimator. The observer was in this way protected from the brilliant luminescence produced during excitation, but was enabled to observe the phosphorescence immediately after excitation had ceased. The comparison slit being set to some suitable reading, the observer recorded upon a chronograph the instant when the two parts of the spectrophotometer field appeared equally bright. By means of a suitable electric contact on the shutter a record was also made at the time when the exciting light was cut off. In this way the time required for the phosphorescent light to fall from its initial value to any given final value could be conveniently measured.

The determination of the instant when the rapidly changing phosphorescence became equal to the constant comparison light would at first appear to be a difficult observation, and one not capable of great accuracy. As a matter of fact these observations were fully as reliable as ordinary spectrophotometric settings, and at these low intensities far less trying to the eye.

The most serious difficulty encountered in these measurements arose from the unsteadiness of the exciting light. When constancy is essential the arc, even under the best of conditions, leaves much to be desired. After numerous unsuccessful attempts to obtain steady conditions we abandoned all special efforts to keep the excitation constant, and arranged to make observations only when the exciting light, either by adjustment or by accidental fluctuation, had reached a certain definite intensity. In order to accomplish this a second spectrophotometer (S_2 in Fig. 31) was used. Light from the luminescent screen was thrown into the collimator by means of a mirror as shown in the figure. The comparison light came from the acetylene flame F after reflection from a mirror and a block of magnesium carbonate not shown in the figure. One observer at the eyepiece of S_2 waited until the intensity of fluorescence reached such a value as to give equality of the two fields, and then, with suitable warning, dropped the shutter C. The second observer at S_1 then made a chronograph record as before described. Numerous determinations, often twenty or more, were made in this way for each point of the curves described below.

A preliminary set of measurements in which the duration of excitation was varied from 3 sec. to 30 sec. showed no variation in the time of decay. We conclude that the full effect of the exciting light is produced in less than 3 sec. In the subsequent experiment the duration of excitation was never less than 5 sec.

TABLE I.

Giving the observed time, in seconds, during which the phosphorescence fell from its initial intensity to the intensity given at the top of the column.

Wave-length.	$I = 100$.	$I = 60$.	$I = 0$.	$I = 10$.	$I = 5$.
0.461 μ				0.458	
0.472		0.00		0.99	
0.483	0.00	0.456	0.745	2.07	7.1
0.497	0.491	0.95	1.63	3.13	
0.512	0.502	1.00	1.80	3.41	10.4
0.528	0.290	0.682	1.49	2.91	
0.535	0.00				
0.547		0.223	0.838	2.55	7.5
0.553		0.00			
0.568			0.302	1.30	
0.572			0.00		
0.592				0.713	4.1

The results of one set of determinations made in this way are given in Table I. and are plotted in Fig. 34. In Curve I. the width of the comparison slit was kept at 100 divisions of its micrometer screw, and the time required for the phosphorescence of any given wave-length to fall from its initial value to this intensity was determined as described above. The curve is obtained by plotting wave-lengths as abscissas and times as ordinates. In Curve II. the width of the comparison slit was 60 divisions; in Curve III., 30 divisions; and in Curve IV., 10 divisions. Observations made at 5 divisions are not included on the plot. . Points lying on the horizontal axis in Fig. 34 were located by determining by trial the wave-length for which there was a balance in the spectrophotometer the instant after dropping the shutter. These points are probably somewhat less reliable than the others.

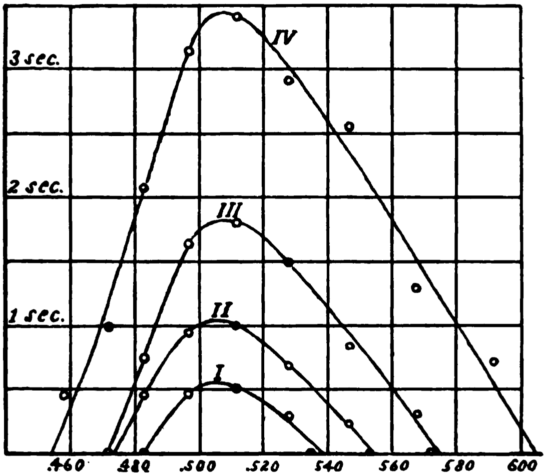

Fig. 34. Curves showing the time required for the phosphorescence to fall from its initial intensity to a given final intensity. The final intensity is kept constant throughout each curve.

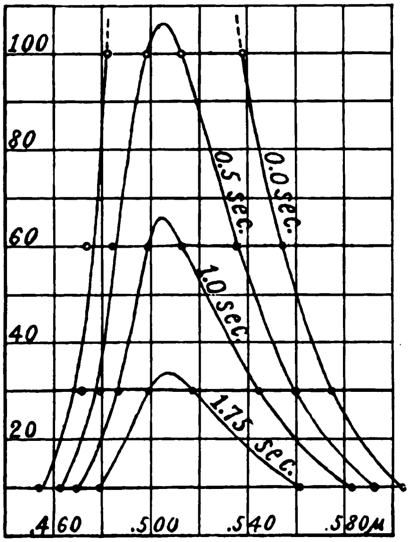

Fig. 35. The phosphorescence spectrum of Sidot blende at different times after the removal of the exciting light.

The significance of these results is better shown by plotting them in a different way. In Fig. 35 wave-lengths are plotted as abscissas as before, but intensities, instead of times, are plotted as ordinates. Each curve in this figure shows the distribution of intensity in the phosphorescence spectrum at some definite time after the removal of the exciting light.

No curves have been plotted for intervals of more than

1.75 sec. after excitation had ceased, since our data furnished so few points for the later curves that their form would be largely a matter of conjecture.[1] As already stated, however, a curve of the type shown in Fig. 34 was determined for an intensity of 5 divisions. The maximum ordinate of this curve was 10.1 sec. and occurred at 0.506 μ — *i. e.*, at the same wave-length as in the case of the curves shown in 34. Comparison with Fig. 32 shows that the maximum of the luminescence spectrum during excitation also occurs at this wave-length. In the case of the green band of Sidot blende we conclude therefore that the maximum of the fluorescence spectrum occurs at the same wave-length as that of the phosphorescence spectrum; and that no change that could be detected by our apparatus occurs in the position of this maximum for ten seconds after excitation has ceased.

Fig. 35 also shows that if any change occurs in the form of the phosphorescence spectrum during decadence, this change is extremely small. In other words the different wave-lengths of the phosphorescent spectrum decay at the same rate. Table II. will show to what extent this conclusion is justified by the data. Each column of this table refers to the wave-length stated at the top, and in it are tabulated the intensities for this wave-length at different intervals after the end of excitation, these intensities being expressed in terms of the intensity at the end of 1.75 sec. as unity. If the phosphorescence spectrum remains absolutely unaltered during decay, all the numbers in this table that lie in a given horizontal line should be equal.

Table II.

Intensity of Phosphorescence at Different Intervals After Excitation Had Ceased, Expressed in Terms of the Intensity at the End of 1.75 *Sec.*

	0.48 μ	0.50 μ	0.52 μ	0.54 μ	0.56 μ
0.0 sec.	7.8 ?			5.2	4.8
0.5 "	3.5	3.3	3.1	3.0	2.8
1.0 "	1.9	2.0	1.8	1.8	1.9
1.75 "	1.0	1.0	1.0	1.0	1.0

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[1] In a series of observations of the kind recorded in Fig. 34 the number of points that could be located was limited both by the difficulty of maintaining constant conditions during the three or four hours of observation, and by the endurance of the observer's eye.

The numbers in Table II. corresponding to 0.0 sec. are uncertain; first, because the observations by which the initial phosphorescence was determined were themselves especially uncertain; and second, because the steepness of the curve (Fig. 35) in the neighborhood of 0.48 μ and 0.54 μ would cause a slight change in the manner of plotting to produce a large change in the ordinates at these wave-lengths. If the ratios tabulated for 0.0 sec. are left out of consideration, the agreement between the remaining ratios, at 0.5 sec. and 1.0 sec. is as close as could be expected. We conclude that, although there is some indication of more rapid decadence at the ultra edge of the phosphorescence spectrum, the probability is that all parts of the spectrum decay at the same rate, and that the form of the phosphorescence spectrum remained unchanged.

While the result obtained in this one case is not sufficient to establish a general law, we are nevertheless of the opinion that the behavior of Sidot blende is typical, and that in no case of phosphorescence is there any change in the form of the spectrum during decadence. In complex cases of phosphorescence we do not imply by this that the phosphorescence spectrum as a whole remains unchanged in form, but rather that the distribution of intensity in each band is unaltered. If the phosphorescence consists of several bands, it is to be expected that the different bands will decay at different rates. In fact Sidot blende itself furnishes an extreme illustration of this, for the violet bands die out in one or two tenths of a second, while the green band persists for hours.

Numerous cases in which the color of a phosphorescent substance seems to change as the phosphorescence dies out at first appear to contradict this view absolutely. We think, however, that all cases of this kind may be shown to belong to one of the two following classes:

1. Cases of real color change. For example, anisic acid at low temperatures, where the phosphorescence changes from blue to greenish yellow.[1] Such cases are probably due to the presence in the luminescence spectrum of several phosphorescence bands, which decay at different rates. In the case of anisic acid the results would be explained by the presence of a brilliant but rapidly decaying

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[1] Nichols and Merritt, PHYSICAL REVIEW, vol. 18, p. 355, 1904.

band in the blue, and a persistent band of smaller initial intensity in the yellow.

2. Cases where the apparent change in color is due to the fact that the color sense in the eye is either weak or entirely absent at low intensities. At very low intensities all colors appear to the eye as gray. However brilliant may be the color of the phosphorescence light initially, it loses this color and changes to a gray or faint white as it becomes fainter. But such a change as this is in the retina, and does not indicate any change in the phosphorescence spectrum. We are convinced that the use of the unaided eye in the study of luminescence may lead to serious errors.

It is interesting to note that attention was called to both of these causes of change of color during decay by the elder Becquerel.[1]

The data of Table I. might also be used to study the law of decay of phosphorescence, *i. e.*, the relation between intensity and time. More reliable results are obtained, however, by studying one wave-length at a time, since the data necessary for plotting a decadence curve may in this case be obtained more quickly and are, therefore, less liable to error due to fluctuating conditions. Experiments dealing with the law of decadence and with the effect of infra-red radiation upon phosphorescence will be described later.

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[1] Ed. Becquerel, C. R., vol. 49, p. 27, 1859; Ann. de Chemie et de Physique. Series 4, vol. 62, p. 20, 1861.

THE JOULE-THOMSON EFFECT IN CARBON-DIOXIDE. I. EXPERIMENTAL.

By Frederick E. Kester.

Historical Summary.

THE original Joule experiments, the aim of which was the determination of the amount of work done against the forces of intermolecular attraction when a gas expands without doing external work, were performed in 1844.[1] The apparatus, used by him, consisted of two copper flasks, each of about 2.2 liters capacity, joined by a pipe and a stop-cock, which opened or closed the connection between them ; the whole was submerged in a water calorimeter. The air having been removed from one of the flasks by pumping to a very low pressure and the test gas having been pumped into the other to a high pressure, it is evident that, upon opening the stop-cock, the expansion of the gas to twice its original volume, took place without the performance of external work. Any fall or rise in the temperature of the gas as a whole must have meant a decrease or an increase in the kinetic energy of its molecular motions with an equal increase or decrease in the potential energy of molecular separation. But, in spite of the facts that initial pressures as high as 22 atm. were used and that the calorimeter was so shaped that the water used was reduced to the smallest allowable amount, no noticeable change in the temperature of the bath occurred. It must be regretted that this apparatus cannot be made sensitive enough to measure the amount of energy changed from one form into the other during the expansion, for here the effect sought is a pure one — no part of the internal energy is expended in external work — an advantage which no other form of apparatus possesses.

It was during a report by Joule, upon these experiments, before the Royal Society in 1844, that Thomson became interested in the problem ; to him is due the porous plug form of apparatus. With it the method employed is to maintain constant gas pressures on the two sides of a plug of porous material, packed tightly into a short length of the gas path. The flow through the plug is then a steady one, of such character that practically no work is done in giving the gas a kinetic energy due to an increase in its stream velocity — the flow is a diffusion process. Here, however, the thermal effect obtained is no longer a pure one ; the difference in the temperatures of the gas before it enters and after it leaves the plug is due both to the work done against molecular attractions and to the difference between the values of the product $p \cdot v$ ($p =$ pressure ; $v =$ specific volume) which exist on the two sides of the plug. This difference is the difference between the amount of work done upon one gram of the gas in forcing it into the porous plug and the amount done by one gram of the gas as it leaves the plug. The product $p \cdot v$ will have different values on the two sides of the plug, not only because the particular gas in use does not follow Boyle's law ; the difference in temperature, caused by the change in the potential energy of the molecules, will of itself establish a difference between the values of the product. Just how large a fraction of the total thermal effect this external factor may become in special cases will be shown later in a discussion of experimental results. I speak of it here at some length in order to make as clear as possible the errors which are liable to affect any theoretical discussion involving (implicitly or explicitly) a separation of the total observed thermal effect into its component parts ; although the whole may have been measured with considerable accuracy, it may not be possible to make this separation with the same nicety.

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[1] J. P. Joule, Phil. Mag. (3), 26, 369, 1845 ; Joule's Scientific Papers, I., 172.

The series of researches carried on by Joule and Thomson,[1] with the porous-plug form of apparatus, extended through the years from 1852 to 1862, and included work on air, oxygen, nitrogen, carbon dioxide, hydrogen and mixtures of two or more of these.

Following the same principle which underlies the porous-plug experiment, Hirn[2] made a series of observations upon the cooling effect experienced by steam (in both the saturated and superheated states) when it expands from various pressures to atmospheric pressure. The expansion in these experiments did not take place through a porous-plug, but through a small opening into a large, well-jacketed space; in order to destroy (partially at least) the high stream velocity resulting from the free expansion, the steam was made to impinge upon a flat surface placed only a short distance in front of the opening through which it expanded.

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[1] Joule and Thomson, Phil. Mag. (4), 4, 481, 1852 ; Phil. Trans., 143, 357, 1853 ; Phil. Trans., 144, 321, 1854 ; Phil, Trans., 152, 579, 1862 ; Joule's Sci. Pap., II., 216 ; Kelvin's Math. and Phys. Pap., I., 333.

[2] G. A. Hirn, Théorie Mech. de la chaleur (3 éd.), II., 387.

Then, returning to the original form of apparatus used by Joule — that of the double flask — Cazin[1] performed a number of experiments upon air, carbon dioxide and hydrogen. In his work, although the form of apparatus was essentially the same as Joule's, the method of experiment was very different and much more complicated. In its main features the method was as follows: With the large stop-cock between the flasks open, the pressure of the contained gas was measured by suitable manometers, and the temperature, brought to the same value in the two chambers, was observed. The stop-cock was closed, a *part* of the gas was pumped from one flask into the other and the flasks and contained gas were brought to the original temperature, under which conditions the new pressures were measured. Then with the stop-cock wide open, the gas was allowed to expand suddenly from the one flask into the other; as soon as the pressures had become equal the cock was closed, and a series of pressure and time readings were taken while the temperatures were brought again to the original value. Finally the stop-cock was opened, the temperatures were brought a fourth time to the same original value and the common pressure was measured. By this last step any loss of gas, which may have occurred during the pumping or expansion, could have been detected. The pressure and time readings were used to indicate the value of the common pressure at the time of opening the stop-cock; the knowledge of this pressure completed the data, from which the state of the gas at each step was determined. The whole process could then be subjected to thermo-dynamic analysis. The relation between this method of procedure and that of Joule's will be readily understood by observing that Cazin measured (implicitly) the changes in temperature of the gas by means of the pressure changes. On account of numerous complications the results of these experiments are open to serious criticism, and in the later discussion of the results of the various researches they will not be considered.

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[1] A. Cazin; Ann. de Chim. et de Phys. (4), 19, 5, 1870.

From the time of Cazin's work no other experimental results upon this problem appeared until those of Natanson[1] were published in 1887. His work was done with the porous-plug form of apparatus, the same in all important features as that of Joule and Thomson. Natanson's observations were made upon only one gas, CO_2, and at room temperature. The method of procedure was to keep the difference of the pressures on the two sides of the plug very nearly the same (about one atmosphere) in all of his experiments and to vary the initial pressure of the gas at will, whereas in the Joule-Thomson researches the pressure behind the plug was kept the same (barometric pressure) and the pressure in front varied. The highest pressure used by Natanson was nearly 25 atm., and between the lowest and this highest pressure he found a decided dependence of the cooling effect of CO_2 upon pressure, whereas Joule and Thomson had been unable to detect (up to 6 atm.) any such dependence in the case of any gas. Natanson, in the report on his work, lays special emphasis upon the remarkable purity of the gas used in his experiments, and criticises the Joule-Thomson results on this ground, though the criticism as made is not a fair one.

In 1898 Witkowski[2] published a report on the determination of the cooling effects in air when it was allowed to expand through a series of porous plugs spaced along a considerable length of tube. Nothing but a review of this article has been available in the libraries consulted; consequently no judgment can be given here concerning the value of the results.

More recently a very interesting determination of the inversion temperature of the Joule-Thomson effect in hydrogen was made by Olszewski.[3] The expansion in this case took place through a small opening into a large space in which the jets and eddies were dissipated into thermal (molecular) motions, as in Hirn's experiments. In the expansion chamber was placed a delicately constructed platinum thermometer coil, and this chamber together with the spiral tube which led the hydrogen to the small jet-opening was submerged in a cooling bath. The temperature of the bath was so adjusted that, after all parts of the apparatus had reached the proper thermal condition and the jet was opened, no change in the resistance of the platinum coil could be detected.

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[1] E. Natanson, Wied. Ann., 31, 502, 1887.

[2] A. W. Witkowski, Rozprawy der Krakauer Akad., math-naturw. Klasse, 35, 282, 1898; Beiblätter, 23, 411, 1899.

[3] K. Olszewski, Ann. d. Phys., 7, 818, 1902.

The present research, the results of which are to be described in this paper, was undertaken at the suggestion of Professor Nichols. It was started in the past academic year (1903–4) in Professor Voigt's division of the Physical Laboratory in Göttingen and the results of this preliminary part of the work were published in January of this year.[1] The general arrangement of apparatus, both in Göttingen and in Ithaca, has been in principle the same as that of Joule and Thomson and of Natanson. One essential difference lies in the use of thermo-electric junctions placed in the gas path, instead of thermometers, for the measurement of the temperature changes. Various important alterations, in the present apparatus, from the design and from the method of manipulation of last year will be mentioned below.

I shall express here my sincere thanks for the valuable suggestions and for the kindly encouragement and direction given to me by Professor Nichols and Professor Merritt. I wish also to thank Professor Moler for many suggestions as to the construction of apparatus. Nothing in my work has been more pleasant than the uniformly courteous treatment which I have found throughout the department.

DESCRIPTION OF APPARATUS.

A general diagram of the apparatus is given in Fig. 1. The gas was obtained in the usual CO_2 cylinders which contain about 20 pounds of liquid CO_2. This quantity is equivalent to 4,500 or 4,600 liters of gas under normal conditions. The great advantages of such a source lies in the high pressures and in the steadiness of the pressure under which the gas is delivered from them: at room temperature the vapor pressure of CO_2 is 55–60 atm. In order to avoid a great decrease in the temperature of the liquid, due to evaporation, the cylinders were placed in a water bath while in use; this was especially necessary when the determinations were made at high pressures, for then the quantity of gas delivered to the apparatus was very great.

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[1] F. E. Kester, Phys. Zeitschr., 6, 44, 1905.

The water vapor, carried along with the gas, was removed by calcium chloride contained in the U-shaped drying tube. Examination of the drying material, when it was thought advisable to inspect the condition of the tube, left no doubt as to the thoroughness of its action; the chloride in the last branch of the tube seemed perfectly dry, and was easily shaken out; that in the first branch (at least that in the top part) was somewhat moist; how far down this state of affairs extended could not be discovered for the material could not be shaken out. The tube was washed out, thoroughly dried and refilled with fresh chloride.

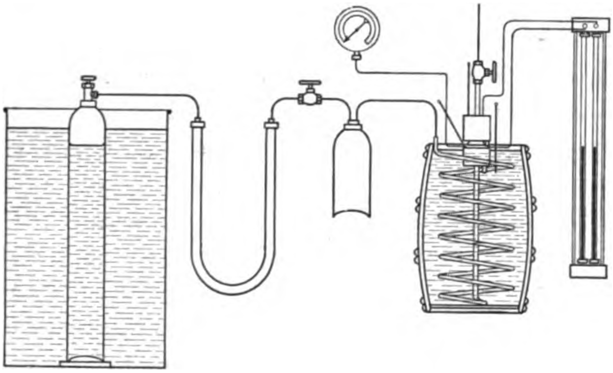

Fig. 1.

The control valve through which the gas next passed is well adapted, by its form of construction, to this use. Its needle is small — about 2.5 mm. in mean diameter — and only slightly conical. The regulation of the pressure in the part of the apparatus beyond it could be made with considerable nicety by means of a short lever arm attached to the hand-grip of the valve.

From the valve, the gas next passed into the small cylinder which served as a pressure equalizing reservoir. Its capacity is 4.3 liters; the volume of this part of the apparatus — from valve to valve — is very nearly 5 liters.

The copper tube, which led the gas from the equalizing chamber up to the porous plug is 10 mm. in inner diameter, 1.25 mm. in wall thickness and about 8 m. long. Before it was wound into spiral form its complete length was threaded with long, spiral, steel lathe-turnings. This was done to break up the possible formation of any well defined stream lines, which would prevent the gas from coming thoroughly into contact with the walls of the tube. The mass of water in which the spiral was submerged was about 100 kg.

After passing through the plug the gas escaped through the second needle valve into the open.

The construction of the nozzle, in the middle of which the porous plug is held, is shown in detail by Fig. 2. The same plug was used for all the experiments of this year's work; it contains 3.4 g. of clean cotton fiber, compressed between two thin perforated disks of steel into a space 15 mm. in diameter and 24 mm. in height. The material immediately surrounding it is the red "vulcanized fiber" which is found so useful in electrical construction. It is inferior to hard rubber in heat insulation, but rubber could not be considered for this purpose because it becomes semiplastic long before it reaches the temperature of boiling water. The small tube which holds the upper steel disk in place is also of this same material. The steel cylinder, which surrounds the vulcanized fiber nozzle, is provided with screw caps as shown; lead washers are used in packing the joints. The thermo-electric junctions are made of steel and constantan wires 0.18 mm. in diameter and are carried by plugs of vulcanized fiber. The wires are cemented in place with a mixture of litharge and glycerine — a cement which serves remarkably well for such purposes. The plugs themselves are held hard upon the seats, cut for them in the steel cylinder, by means of steel encircling rings, each of which is provided with a slot on one side and a set screw diametrically opposite. Pressure tubes lead into the gas path at points indicated in the drawing; one is joined to the pressure gauge (see Fig. 1); the others to the mercury pressure-differenee manometer. Finally the two oil cups, one surrounding the lower part of the nozzle, the other the upper part, are held in place as shown. Each of these baths as well as the large water bath is provided with a stirrer; a small motor furnishes power for all of them.

Electrical heating coils were used in the various baths to maintain constant temperatures when determinations were made above room temperature; ice, in the large water bath, and copper tubes, in the oil baths, through which cold salt-water flowed, were used in the determinations at 0° C.

This part of the apparatus is in design quite different from the nozzle used last year in the preliminary part of this research. The changes were made in order to accomplish (1) observations at higher temperatures than would have been possible of attainment with hard rubber; (2) the insertion of the thermal junctions into place without the necessity of unsoldering and resoldering after they had been calibrated; (3) a definite control of temperatures about the two parts of the nozzle.

The whole apparatus was designed to work up to a pressure of 50 atm. with a factor of safety of at least 2 in all parts. The highest pressure at which determinations were made was 41 atm.

A set of the usual gas analysis pieces was used to determine the amount of impurity in samples of the gas taken from the apparatus after a determination was finished. A solution of KOH was used to absorb the CO_2 and the residue was then measured.

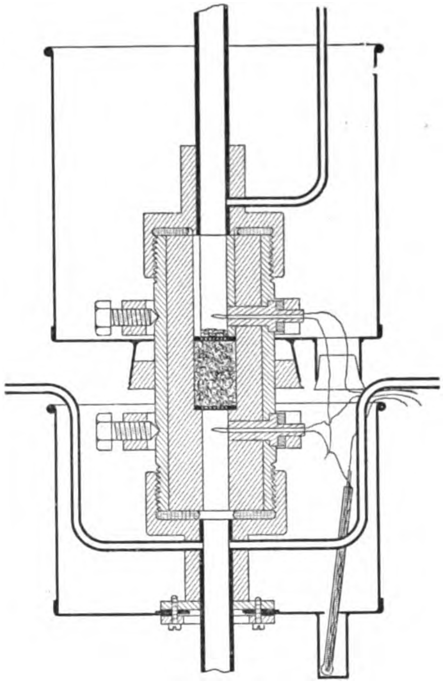

Fig. 2.

The electrical circuits are shown diagrammatically in Fig. 3. The method involved is that of the potentiometer somewhat modified. The two thermo-electric junctions in the gas path constitute a couple for the measurement of the difference of temperatures above and below the porous-plug; the junction in the bath and one of the others serve to measure the difference between the bath temperature and the gas temperature. The steel wires *I* are brought to a common junction; the constantan wires *C* are joined one to each of the three wires which lead to the switch *S* and to the potentiometer wire *AB*. To avoid, as far as possible, junctions between dissimilar metals all lead wires and the wire *AB* are of constantan; an important advantage results also from the fact that the resistance of *AB* remains constant even though the room temperature vary considerably.

The closed circuit, of which the potentiometer wire is a part, consists of a dry cell as a source of current, a variable resistance (part of which is a liquid resistance for fine adjustment of current strength),

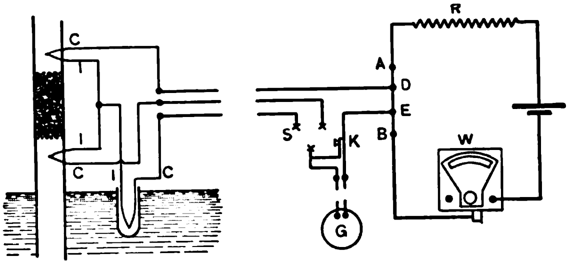

Fig. 3.

the potentiometer wire *AB* and a Weston voltmeter used as an ammeter. The sensitiveness of this instrument is such that a full scale deflection is caused by a current somewhat less than 0.01 amp. In order to use it in the circuit, a connection is inserted so that the current flows through only the moving coil (of about 70 ohms resist.).

The switch *S* deserves special notice. In circuits where the electromotive forces are as small as those which are handled here (the greatest value of the e.m.f. in this part of the circuit during observations was about 0.00007 v., and the aim, during the construction of the circuits, was to keep the stray e.m.f.'s within one five-hundredth of this maxim) no ordinary form of switch can be used satisfactorily even when extreme care is taken in the thermal isolation of the working parts. The construction of the switch is shown in Fig. 4; an ordinary three-way glass stop-cock was used for the purpose, and mercury serves as the conducting material.

No description will be necessary to make the drawing clear, unless it be such as will call attention to the precaution of sealing thin-walled glass tubes onto the heavy ones where they entered the mercury jacket. The three constantan wires which lead to the switch enter the tubes from above and dip into the mercury. This use of stop-cocks as electrical commutators and switches is due to des Coudres.[1]

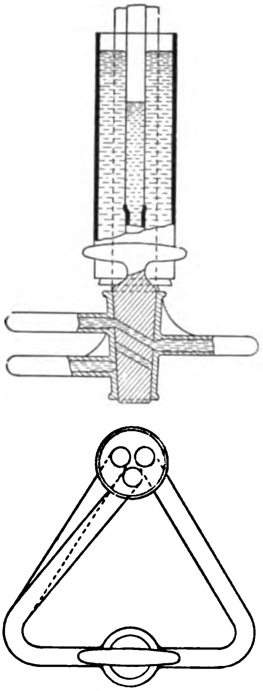
Fig. 4.

The galvanometer G is of the moving coil type, It is the one which was constructed in this laboratory by White and was fully described by him last year in this REVIEW.[2] At all soldered junctions, even where wires of the same metal joined and especially where dissimilar metals joined, precautions were taken to keep corresponding junctions at the same temperature. But in the galvanometer different materials were used in the various parts, and this precaution could not readily be taken. Trouble from this source was avoided by using a piece of constantan wire as a short-circuiting key K. With S open and K closed, a deflection of the galvanometer needle usually occurred; the steady reading of the galvanometer with S and K in these positions was taken as the zero point of the apparatus at the time. A long study of the circuits showed that, with a pair of the steel-constantan junctions submerged in the same bath of mercury as near each other as possible, with no current flowing in the potentiometer wire AB and with S properly closed, the galvanometer deflection never differed from that obtained by opening S and closing K as much as the maximum error, mentioned above, would allow. This method of taking the zero point was, therefore, justified.

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[1] Th. des Coudres, Wied. Ann., 43, 673, 1891.

[2] W. P. White, PHYS. REV., 19, 305, 904.

CALIBRATION. MANIPULATION. SOURCES OF ERROR.

No great amount of care was necessary in order to measure gas pressures and pressure differences with sufficient accuracy. The observations of last year upon CO_2 at room temperature, showed that the dependence, if any, of the thermal effect upon pressure is so slight that the use of a pressure gauge with even tolerably large scale errors would have been allowable, provided that the mechanism be delicate enough to indicate small changes in pressure. The instrument used in the present apparatus has a range of 1,000 lbs. per sq. in. and a least count of 4 lbs.; motions of the pointer corresponding to pressure changes of 0.5 lb. could readily be detected and slight tappings on the gauge insured a corresponding freedom of motion of the mechanism.

The mercury pressure-difference manometer was read by means of clips which fit nicely to the glass tubes and reach over to a wooden meter bar between the tubes. An error of as much as 1 mm. in the determination of a total height of mercury of 700 or 800 mm. would have been less serious than the errors which could not be avoided in the temperature measurements.

Each of the three baths was provided with a Baudin thermometer of 100° range subdivided to fifths of a degree; readings to fiftieths could easily be made. The stem of each one was calibrated throughout its length and corrections were calculated from this calibration and from determinations of the fixed points. The thermometer in the large bath was always submerged to a point only a little below the top of the mercury thread; therefore no stem correction (due to a difference between the temperature of the stem and that of the bath) was necessary for this one. Auxiliary thermometers were tied to the stems of the other bath thermometers and stem corrections, calculated from the readings of the auxiliaries and from the lengths of mercury threads out of the baths, were applied.

The first step made in the calibration of the electrical part of the apparatus was to check the accuracy of the Weston instrument scale at small intervals. This was done with the aid of a potentiometer. The departures of the ammeter readings from a proportionality to the strengths of current which produced them was in no case greater than 0.2 of a scale division.

In the calibration of the thermal junctions three Baudin thermometers, each of 12° range, subdivided to fiftieths of a degree, and a Golaz thermometer, of similar construction, were used. The Baudin thermometers (0°–13°, 12°–23°, 22°–33°) were sent to the National Bureau of Standards for comparison with the standard thermometers of that institution. After their return to this laboratory the Golaz was carefully compared with the Baudin of 12°–23° range and these two were used in the actual calibration of the working thermal junctions. By means of a magnifying eye-piece, which was made for this purpose, thermometer readings were estimated to 0°.001; errors due to jumping of the mercury threads were avoided as far as possible by taking readings while the temperatures were slowly rising.

It was, of course, not to be expected that accuracy such as this could be attained in baths when the temperatures were far from that of the room, and as the junctions were to be used in determinations at temperatures from 0° to 100° some method was necessary by which a careful calibration at room temperature could be extended. This was done by use of an auxiliary thermal couple (the working junctions could not be used on account of the length of wires necessary). One junction of the couple was kept at 0° C. while the other was carried over the range of temperatures from 0° to 100°. For this part of the calibration the potentiometer wire (*AB* of Fig. 3) was made of such length that the points *D* and *E* were 100 cm. apart. The resistance of this length of wire having been measured and the constant of the ammeter being known, it was possible to reduce the ammeter readings to micro-volts. The parabola

$$e = a \cdot t + b \cdot t^2$$

was then fitted to the observations. The third column of the following table gives the e.m.f.'s calculated from this equation with $a = 50.8_4$ and $b = 0.021_9$. The significance of the columns of residuals will be better understood when it is stated that one tenth of an ammeter division is equivalent to about 4 micro-volts of thermo-electromotive force.

Temperature (Degrees).	E.M.F. (Microvolts).		
	Observed.	Calculated.	Residuals.
18.78	965	962	+3
0.08	3.0 (?)	4	−1
2.07	101	105	−4
2.14	102	108	−6
7.23	364	369	−5
7.29	367	372	−5
7.40	375	377	−2
11.77	596	601	−5
11.80	601	603	−2
11.81	601	603	−2
21.27	1,091	1,091	
21.24	1,087	1,089	−2
21.20	1,087	1,087	
26.03	1,337	1,339	−2
25.96	1,336	1,335	+1
25.91	1,335	1,332	+3
31.91	1,644	1,645	−1
31.72	1,635	1,636	−1
31.59	1,625	1,629	−4
99.52	5,276	5,276	

From the above equation we have as the thermo-electric power of this particular steel and constantan

$$de/dt = a + 2bt = 50.8_4 + 0.043_8 \cdot t = 50.8_4 (1 + 0.00086_2 \cdot t)$$

The determination of the "temperature coefficient" (0.00086_2) of thermo-electric power of these metals was the aim of this part of the work.

The actual calibration of the working junctions at room temperature was next made. Two mercury baths were used for this purpose; the mercury was contained in two small, cylindrical Dewar bulbs submerged side by side, nearly to their tops in the same bath of water. The thermal junctions were protected with thin coatings of collodion and one was placed in each of the mercury baths close to the bulb of one of the two thermometers mentioned above. The long potentiometer wire was replaced by a short constantan wire 1 mm. in diameter, and *DE* was made 14 mm. (resistance about 0.009 ohm).

Fig. 5 shows the results of a calibration, made before determinations on the thermal effect had been begun. Only one calibration was made before the determinations because this one checked so closely two calibrations of a couple, which was broken before it could be used, that more were considered unnecessary. The intention was to make a second calibration after all determinations had been finished, but in removing the junctions from their places, one of the small plugs was broken; recalibration was therefore impossible. The fact that the curve does not pass through the origin of coördinates is easily explained by a change in the thermometer corrections after comparison; with both junctions in the same mercury bath, with no current in the potentiometer and with the switch *S* properly closed no deflection of the galvanometer occurred. The working curve was therefore drawn to the same slope as the calibration curve and made to pass through the origin.

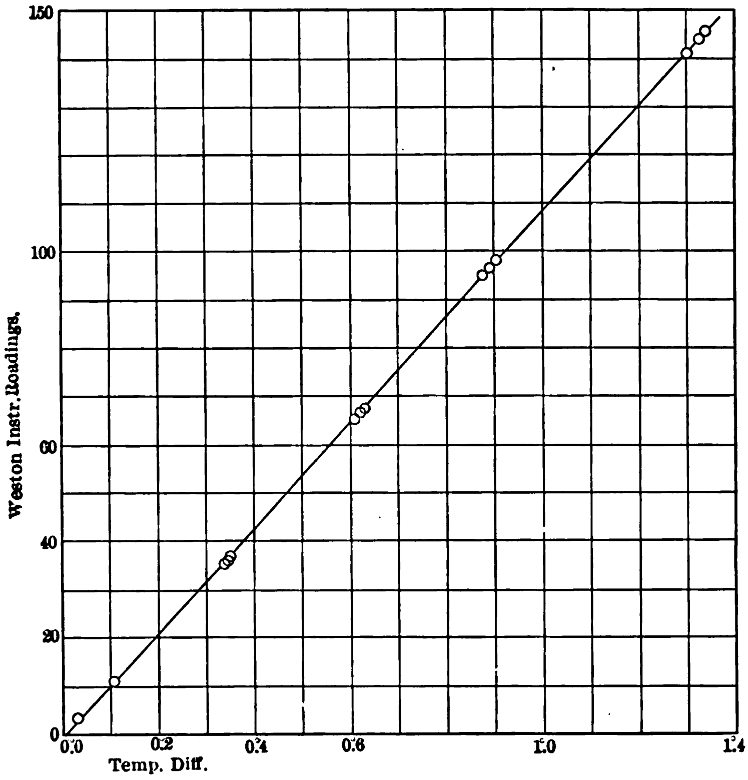

Fig. 5.

If w be used to represent the ammeter reading and τ the *difference* in the temperatures of the thermal junctions, the working curve is given by the equation

$$\tau = 0.00925 \cdot w$$

when the mean temperature, t, is 20°.3 C. Then from the work on the auxiliary couple we have

$$\left(\frac{w}{\tau}\right)_t = \left(\frac{w}{\tau}\right)_0 (1 + 0.00086_2 \cdot t).$$

From these we find that

$$\left(\frac{\tau}{w}\right)_0 = 0.00941$$

and therefore that

$$\left(\frac{\tau}{w}\right)_t = \frac{0.00941}{1 + 0.00086_2 \cdot t},$$

which enables us to transfer ammeter readings into temperature differences for any mean temperature. The sensitiveness of the ammeter, immediately after the calibration was completed, was found to be $5.83_6 \times 10^{-5}$ amp. per division. The sensitiveness was afterwards taken at intervals of several days; changes could be noticed (due apparently to weakening of the magnetic field) but they were so slight as not to affect the calibration.

After the calibration the collodion was dissolved from the junctions and these were put into their places in the nozzle.

In the manipulation of the apparatus three persons were necessary. It was the duty of the first to attend the control valve and by careful adjustment to maintain a constant pressure in the part beyond; the second person controlled the bath temperatures and read the thermometers and the pressure difference manometer; the third attended the galvanometer and ammeter readings.

In order to make a determination the baths were put into the proper condition, the pressure was brought to the desired value and the exit valve was opened until the pressure difference was about one atmosphere. The large water bath was kept as nearly as possible at constant temperature and the oil baths were brought to temperatures which were indicated from time to time by the electrical readings. The time necessary for a determination varied from fifteen minutes to an hour; in several cases even a longer time elapsed before steady conditions were attained.

In general the pressure difference, under which a determination was made, was not exactly one atmosphere. Correction was made to this unit by assuming a proportionality of the thermal effect to pressure difference — a law firmly established by the work of Joule and Thomson and again by that of Natanson.

The control of temperatures of the oil baths was a source of difficulty — especially in the determination at 0° C., for at this temperature it was necessary to use a flow of cold salt water through copper tubes submerged in the oil and the control was not an easy one. However, a determination was continued until the proper temperature control had been maintained sufficiently long to insure either a negligible or a calculable error due to this source. To obtain data from which approximate errors could be estimated from known errors in the bath temperatures, large changes in these temperatures were intentionally made from time to time and the resulting effects upon the temperatures of the gas stream were noted.

Of all the determinations which were made, two or three were discarded because the necessary corrections would have been too serious; four of the others were corrected, one to the extent of 0°.015, the other three by amounts not exceeding 0°.010.

It might seem, on first thought, that serious error would be caused by conduction of heat through the porous plug and around the plug through the material of the nozzle. But this transfer is at most only a small thing, and moreover is of such character as to eliminate itself; for the heat given up by the gas stream between the lower thermal junction and the plug will be almost exactly equal to that taken up by the stream in the corresponding region above the plug (the symmetry is broken only by the thin layer of gas between the main body of the nozzle and the small tube of vulcanized fiber which holds the upper steel disk in place).

During the determinations at high temperatures it was necessary to heat the gas before it reached the large spiral in order that it might enter the nozzle at, or very nearly at, the temperature of the bath. The heating was accomplished by applying a Bunsen flame, protected from air drafts, to the copper tube between the pressure equalizing cylinder and the bath. This method of heating cannot be made a very steady one and some fluctuations of temperature remained after the gas had passed through the spiral. The potentiometer settings were made more difficult on this account, but a steady watch was kept on the galvanometer behavior and it was found that the ammeter readings taken when the fluctuations were small were consistent with each other and also that at these times the difference between the temperature of the bath and that of the gas as it entered the nozzle was small.

RESULTS.

Determinations were first made at room temperature, the gas pressure being changed from one determination to another with the intention of finding the law of dependence of the thermal effect upon pressure. The results, as plotted from time to time, began to trace, with more or less certainty, a line parallel to the axis of pressures. The line was very nearly a verification of the results of last year, except that there was no indication of a decrease of pressure until a pressure of 41 atm. was reached. Here the result was considerably lower than those preceding. It was noticed however that the gas analysis, which was made at the end of the determination, indicated a higher percentage of impurity than any of the previous analyses had shown (see determination X. in the table below). It was then decided to delay the experiments and to make a search for purer gas.

The gas, which had been used up to this time, showed amounts of impurity varying from 4 or 5 per cent. (by volume), when taken from a full cylinder, to about 0.2 per cent. when from an empty one; the amount of impurity *gradually* decreased as the gas was used from the cylinders. Complete analyses of the gas were not made, but delicate tests for H_2S and for SO_2 gave negative results. These were considered possible components — the gas came from natural springs — and tests for them were essential because, if present, they would have been absorbed by KOH and would not have appeared as impurities in the partial analyses. Also a test for oxygen gave negative results, showing that the impurity was not air.

No better gas was found, however, and it was decided so to choose the cylinder, which was to furnish the gas for any determination, that two or more results could be obtained, at a given pressure and temperature, with amounts of impurity differing as widely from each other as possible. By this procedure a dependence of the thermal effect upon impurity could be determined, and the thermal effect for pure CO_2 could be found by extending the curves back to the axis of no impurity (see Fig. 6).

This was done and the results of the observations at various pressures and temperatures are contained in the following table. The gas

No.	Date.	Percentage Impurity.	Mean Pressure (atm.).	Mean Temperature.	Pressure Difference (cm. Hg).	Temperature Difference.	Same Corrected on Account of Bath Temperatures.	Temperature Difference per Atmosphere Pressure Difference.
XVI.	5/17	0.32	7.6	$-0^{\circ}.5$	68.6_6	$1^{\circ}.31_6$	$1^{\circ}.32_6$	$1^{\circ}.46_7$
XV.	5/11	0.32	7.6	$-0\ .6$	71.1_7	$1\ .37_1$		$1\ .46_4$
XI	5/4	2.1	7.6	$+0\ .8$	73.2_0	$1\ .32_8$		$1\ .37_9$
								1.39_6 at -0.6
XII.	5/9	0.28	14.4	$-0\ .4$	69.6_0	$1\ .34_6$		$1\ .47_0$
XIV.	5/11	0.75	14.4	$-0\ .6$	69.4_8	$1\ .34_3$	$1\ .32_8$	$1\ .45_5$
XVII.	5/17	0.20	21.2	$-0\ .6$	69.1_5	$1\ .33_2$		$1\ .46_4$
XIII.	5/9	0.72	21.2	$-0\ .6$	72.7_0	$1\ .36_9$		$1\ .43_1$
XVIII	5/18	1.7	26.4	$-0\ .5$	71.2_0	$1\ .36_3$	$1\ .36_7$	$1\ .45_0$
II.	4/19		7.6	$20\ .4$	76.7_3	$1\ .19_9$		$1\ .18_8$
VII.	4/20	1.5	7.6	$20\ .4$	74.5_8	$1\ .14_0$		$1\ .16_1$
VIII.	4/25	0.23	10.8	$20\ .5$	73.6_9	$1\ .16_1$		$1\ .19_7$
III.	4/19		14.4	$20\ .4$	76.1_7	$1\ .17_0$		$1\ .16_7$
IV.	4/19	0.20	21.2	$20\ .4$	76.5_8	$1\ .17_7$		$1\ .16_8$
V.	4/19		25.2	$20\ .4$	75.7_6	$1\ .18_6$		$1\ .19_0$
IX.	4/25	0.89	27.4	$20\ .4$	76.1_2	$1\ .16_4$		$1\ .16_2$
XXI.	5/19	0.24	34.2	$20\ .4$	71.1_3	$1\ .11_8$		$1\ .19_4$
XIX.	5/19	1.1	34.2	$20\ .4$	76.8_8	$1\ .16_4$	$1\ .17_1$	$1\ .15_7$
XX.	5/19	0.45	41.0	$20\ .4$	75.3_6	$1\ .17_4$		$1\ .18_4$
X.	4/25	2.2	41.0	$20\ .4$	75.8_8	$1\ .13_2$		$1\ .13_4$
XXII.	5/24	0.17	7.6	$39\ .5$	75.2_4	$1\ .03_3$ (?)	(Empty Cyl.)	$1\ .04_1$ (?)
XXIV.	5/24	0.24	7.6	$39\ .5$	76.3_0	$1\ .04_8$		$1\ .04_3$
XXIII.	5/24	2.1	7.6	$39\ .5$	75.5_0	$1\ .02_0$		$1\ .02_7$
XXX.	6/2	0.22	14.4	$59\ .5$	76.2_5	$0\ .95_6$		$0\ .95_3$
XXVI.	5/26	1.3	14.4	$59\ .5$	75.1_4	$0\ .93_3$		$0\ .94_4$
XXIX.	6/2	1.3	14.4	$59\ .5$	76.1_6	$0\ .95_0$		$0\ .94_8$
XXXI.	6/15	0.42	14.4	$79\ .5$	74.3_9	$0\ .85_0$		$0\ .86_8$
XXXIII.	6/16	0.20	14.4	$96\ .6$	74.0_0	$0\ .74_7$		$0\ .76_7$
XXXII.	6/16	1.8	14.4	$96\ .5$	77.1_4	$0\ .82_2$		$0\ .80_6$

presures and temperatures tabulated in it are the averages of the two values of each on the two sides of the porous plug. The last column gives the corrected thermal effects — corrected where necessary, on account of errors in one or the other of the bath temperatures, and also on account of the pressure-differences. These corrected values are plotted as ordinates of Fig. 6 with corresponding percentages of impurity as abscissas. The values of the thermal effect for pure CO_2 as indicated by the lines of Fig. 6 are then plotted as ordinates in Fig. 7, with corresponding temperatures as abscissas.

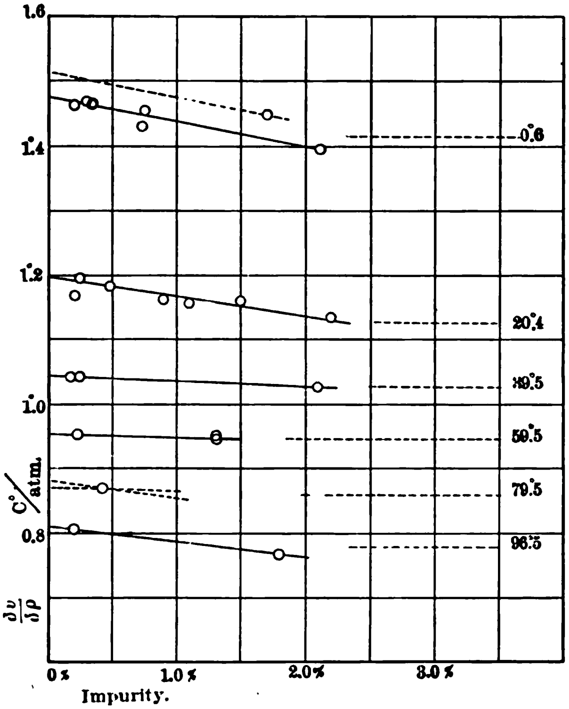

Fig. 6.

For the results obtained at 20° C. the lines of Fig. 6 intersect the axis of no impurity at nearly the same point for all pressures, 41 atm. being the highest pressure reached at this temperature. All except three of the results obtained at 20° are plotted in Fig. 6. No analyses of the gas were made for them (they were obtained before any serious dependence upon impurity was suspected). The determination at 0° C. exhibited the same peculiarity until a pressure of 26 atm. was reached. The result at this pressure gives a point on the impurity diagram considerably above the line which shows the dependence of the thermal effect upon impurity. In the results taken, both at 20° C. and 0° C., there seemed to be no regular dependence of the effect of impurity (upon the observed thermal effect) upon pressure. Accordingly the thermal effect for pure gas at 26 atm. pressure was assumed to be that indicated by a line drawn parallel to the line which represents the other results at the same temperature.

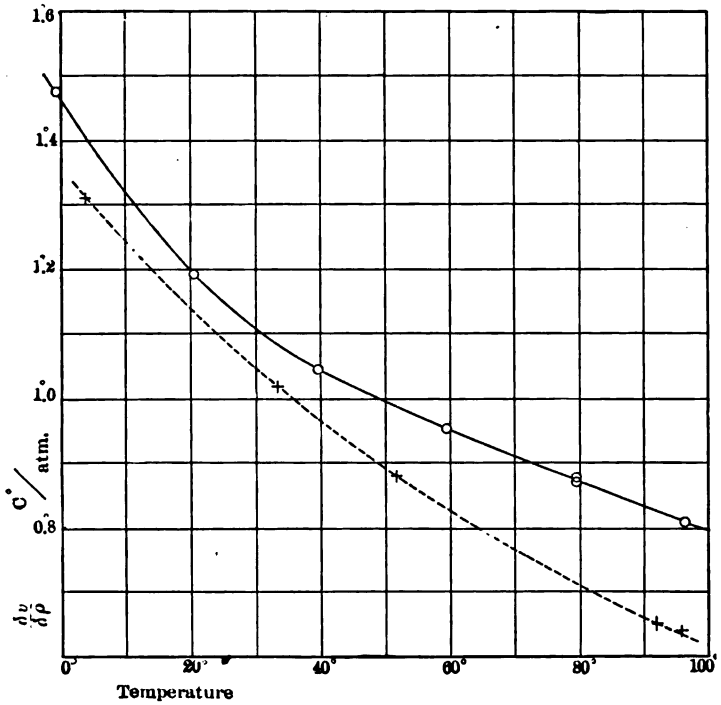

Fig. 7.

Several trials were made at 0° C. to reach higher pressures than this. CO_2 condenses at about 35 atm. when its temperature is 0°, and it had been hoped that determinations could be carried to within 3 or 4 atm. of this point. The behavior of the electrical circuits seemed to indicate that condensation of the gas occurred at the control valve, due to the severe cooling there. If this did occur it was, of course, present also in the case of determinations under high pressures at 20° C.; but at 20° the large copper spiral was able, probably, to cause a complete re-evaporation of the small globules of liquid. The determination at 26 atm. was made possible only by the application of a Bunsen flame to the copper tube just in front of the valve. Very likely the use of a spiral heating tube at this point would have made work at higher pressures possible, but, with the determinations at higher temperatures still to be made, there was no time for the necessary changes.

Of the three results obtained at 80° C. only the last one was kept. The other two were obtained under such unfavorable heating conditions that the behavior of the electrical part of the apparatus did not insure a great amount of confidence in them. The simple application of a Bunsen flame to the small copper tube just in front of the large water bath was found to be quite satisfactory in the determinations at 40° and at 60°, but when the heating became as vigorous as was necessary at 80°, this alone was not satisfactory. The behavior of the apparatus indicated serious irregularities in the effect of the flame, due perhaps to the fact that the gas in passing through the tube came more and less thoroughly into contact with the heated walls. With this explanation in view a corresponding remedy was applied. A length of 25 or 30 cm. of the tube at this place was filled with lathe turnings which served to stir the gas as it passed through the heated portion. With this precaution the observations at 80° and at 97° were fully as satisfactory as those at 60° had been.

An attempt was made, after the determinations at 97° were obtained, to add others at 80°, but a series of mishaps rendered these impossible. The most serious was the development of leaks at the nozzle, caused by the change from a high temperature to a lower one — the lead packing has a much greater coefficient of expansion than the steel of the nozzle. A repair of the leaks made necessary the removal of the thermo-electric junctions, but the plugs which carried them had become so firmly fixed in their places by the action of the high temperatures upon the packing materials that one of them was broken. This made even a recalibration of the junctions impossible. Determinations were discontinued. I may state here — merely as a fact of observation — that all of these accidents occurred while I was using the thirteenth cylinder of gas.

Since only one satisfactory determination was obtained at 80° the best indication, obtainable from it as to the magnitude of the thermal effect for pure gas at this temperature, is that given by the pair of dotted lines, drawn through the point which represents it in Fig. 6, one parallel to the line of results at 60° the other parallel to that at 97°. With this treatment the absence of other results at 80° increases the uncertainty (already present on account of errors of observation and of control) by an amount less than 0°.01.

The variations in the slope of the impurity lines from one temperature to another is a source of considerable concern. The indication of the results up to 60° is that the effect of the impurity becomes less as the temperature increases, but the line of results at 97° does not fulfil this indication. An interpretation of the variation of slope of the lines is offered by the results at 0° and at 20°. At either of these temperatures the determinations which were obtained with the purest gas are fairly consistent with one another — there is only one exception to this statement; result IV., taken at 20°, falls low. On the other hand the results at higher percentages of impurity are not consistent; especially is this true at 0°. So far as records of the determinations are concerned the latter results are just as trustworthy as the others. An attempt to represent the effect of impurity at each of the various pressures, say at 0° C., results in a series of lines whose slopes differ almost as much as do the slopes of the lines from one temperature to another. The only interpretation, then, which the results warrant, is that the impurity is not the same gas or gases in the various determinations. Unfortunately a complete analysis of the impurities was not made for each sample of gas taken from the apparatus. It is fortunate, however, that for almost all temperatures, results were obtained with very pure gas; the distance over which extrapolation is necessary in order to determine the thermal effects for pure gas is not a great one; the errors introduced by the uncertainty in the slope of the lines are, therefore, not serious.

The dependence of the thermal effect upon impurity is a part of an entirely separate problem — that of the Joule-Thomson effect in mixtures of gases — upon which some work was done by Joule and Thomson themselves. I hope to be able to take up this problem, with such modifications of the present apparatus as will be necessary, in order to verify and to make more complete the experimental results at present available. Recent developments in the theory of gas mixtures have made work in this region even more important scientifically than it was in the past century.

In a discussion of the results of the present research it is necessary to call attention to discrepancies between them and the results of previous researches. The preliminary results of last year are not wholly in accord with those of this year. The line

$$\frac{\delta\vartheta}{\delta p} = 1^\circ.19 - 0.0015 \cdot p$$

which was found to represent those obtained last year at 22° C. indicates values for low pressures which are tolerably consistent with the indication of the curve of Fig. 7 for the same temperature. For high pressures the discrepancies are serious and in view of the facts that, in the preliminary work, the amounts of impurity in the gas were not followed closely and that it was impossible to maintain proper temperature control about the nozzle, it is necessary to discard the results of last year in comparison with the present ones.

Considering then the work of Natanson, whose determinations were all made at room temperature (20° C.) and at pressures ranging from 1.5 atm. to nearly 25 atm., it is to be noticed first that the equation, given by him as a representation of his results,

$$\frac{\delta\vartheta}{\delta p} = 1^\circ.18 + 0.0126 \cdot p_m$$

where p_m is the average value of the pressures on the two sides of the porous plug, really does not represent them fairly. The values of the thermal effect plotted as ordinates, with corresponding values of p_m as abscissas, trace with considerable certainty a curved line which starts at about 1°.23 and rises, with steadily increasing slope as the pressure increases, to a value of about 1°.50 at 25 atm.

This very marked dependence upon pressure is not verified by the results of the present research. In the determinations made this year no dependence upon pressure was shown by the results at 20° although the pressure was carried as high as 41 atm.; and at 0° no dependence was found until a pressure of 26 atm. was reached; here the result indicated an increase in the thermal effect over the values at lower pressures. The result just mentioned is isolated and was, moreover, obtained under considerable difficulty; its indications must therefore, in all fairness, be rated as somewhat doubtful. However, in another paper further experimental evidence, deduced from Andrews' work on the compressibility of CO_2, will be given, which will tend to indicate again that such a change is altogether probable at this pressure.

To account for the discrepancy between Natanson's results and my own is not easy. There appears to be only one explanation and that is not entirely satisfactory; it rests upon the fact that, in his apparatus, the large copper tube, through which the gas passed before reaching the porous plug, was closely packed with lathe turnings in order to provide greater surface with which the gas would be brought into contact. The use of more turnings than are sufficient to bring the gas thoroughly into contact with the wall of the tube would seem, however, to be detrimental; there is very little chance for conduction of heat into the interior of the tube by the turnings for they touch the walls and each other only in small points; moreover, if the packing of these turnings was as close as Natanson's description indicates, it is to be expected that a fall of pressure would result from the obstruction offered to the flow of gas, and a fall of pressure means a Joule-Thomson effect of corresponding magnitude. If, therefore, some cooling of the gas, due to this cause, did occur, in all probability the gas entered the plug at a temperature lower than that of the bath, for it is not to be expected that the bath could remove the effects of the fall of pressure which occurred in the last end of the tube. Whether or not such an explanation will account for the total apparent increase in the thermal effect observed by Natanson and for the form of curve, which his results trace, cannot be determined.

In order to compare more readily the results obtained by Joule and Thomson with those of the present piece of work I have copied theirs in the following table; the results are corrected, however, to the basis of 1 atm. difference in pressure above and below the porous plug. The corrections, which had already been made by them, covered errors due to influence of the bath upon the gas stream and reduced the observed thermal effects to the basis of pure CO_2. The latter was made on the assumption that each component of the mixture maintained its own individual thermal effect and was entirely independent of the other component; this assumption was not considered by them to be a correct one — in fact it had been proven experimentally to be false — consequently the last column of the table cannot be considered to be completely corrected. The dotted line of Fig. 7 represents these results.

The Joule-Thomson Results.

Gas Components.		Bath Temp.	Press Diff. in. (Hg).	Obs. Cooling Effect.	Mean Temp.	Corrected Cooling Effect. (1 atm.)
CO_2.	Air.					
96.5 %	3.5 %	7°.4	164.1	6°.72	4°.0	1°.31
98.2	1.8	35 .6	127.5	4 .19	33 .5	1 .02
99.2	0.8	54 .0	146.0	4 .18	51 .9	0 .88
97.9	2.1	93 .5	167.2	3 .42	91 .8	0 .65
98.3	1.7	97 .5	151.0	3 .11	95 .9	0 .64

The discrepancies between these results and my own are very pronounced throughout the range of temperatures used, but are especially so at the higher temperatures. It is at once evident that the incompleteness of the corrections for impurity cannot explain such differences; if, however, data for completing these corrections were available the gap would be narrowed by the process.

In the present apparatus there seems to be only one possible explanation of the discrepancies. There is a possibility of a flow of gas from the region below the porous plug to that above by another path than the porous plug itself. A screw packing (not shown in Fig. 2 on account of complication of the drawing) was provided around the middle of the vulcanized fiber nozzle — between it and the surrounding steel cylinder — in order to prevent any gas from leaving the lower region by flowing outward along the plug which carries the lower thermal junction, then upward between the fiber nozzle and the steel cylinder, and into the main gas stream again, along the plug, which carries the upper junction. Any flow of gas through this packing would be a diffusion process and, if adiabatic, would not affect the accuracy of results; however there is danger that such a flow may be far from adiabatic in character. At high temperatures that part of the steel cylinder between the two oil baths is exposed to air which is lower in temperature than the baths; the error would, therefore, increase the observed cooling effect. This explanation will not account for the discrepancies between the two curves at low temperatures. Moreover the danger here is not as great as it seemed, at first glance, to be. The part of the apparatus from the top rim of the barrel to a point above the upper oil bath was enclosed in heavy wrappings of cloth and the air temperatures in this enclosure, even at points some distance from the baths, were only ten or fifteen degrees below the bath temperatures. The protection of this part of the steel cylinder from the surrounding air is better than the drawing of Fig. 2 indicates; the flange on the bottom of the upper oil cup is deeper than is there shown; it extended, in the determinations at low temperatures, to within a short distance of the oil in the lower bath, and in those at 80° and 97° the hot oil softened the rubber ring, which supports the upper cup, so that it moved down and rested on the steel ring which holds the lower thermal junction in place. Furthermore there is considerable experimental evidence leading to the conclusion that errors from this source were not serious; *e. g.*, when the results were compared and this source of error was under consideration, it was thought that an explanation could be found here for the change in slope of the impurity line at 97° (Fig. 6). Errors in temperature of the oil baths would have had considerable influence upon that part of the gas which may have flowed along this by-path. But the records of the observations at this temperature show that such errors in bath temperatures as were present and also the change in temperature of the air in the enclosure under the cloth wrappings would have had a tendency to decrease the slope of this line rather than to increase it. Finally an examination of the packing, described above, after the apparatus was dismounted, showed that it was hard and firm, and, although it is impossible to say that no gas leaked around by this path, all available facts indicate that the amount was not such as would seriously affect the results.

On the other hand, there are, in the Joule-Thomson determinations, two possible sources of error which may account for the discrepancies between the two sets of results. A study of the descriptions and drawings of their apparatus shows a possibility that the gas pressure above the porous plug was not barometric pressure as they assumed it to be; the gas, after it escaped from the plug, passed through a pipe into a gas holder. The dimensions of this pipe are not given, but from the drawings of their apparatus and from descriptions of other parts I judge that it was a 2-in. pipe; the length is altogether uncertain. There was, moreover, at one point of the pipe a large stop-cock — dimensions uncertain. In view of the fact that the stream velocities varied from 2 to 3 feet per second (assuming the pipe 2 inches in diameter) it seems possible that some appreciable fall in pressure occurred in this pipe and stop-cock. An excess over barometric pressure would have made the pressure difference, under which an experiment was performed, less than that which their mercury pressure gauge indicated. A more serious error would result from the effect of pressure upon the reading of the thermometer which was placed in the gas path just above the porous plug. Each of the errors resulting from this cause would make the apparent thermal effect (reduced to a pressure difference of 1 atm.) smaller than the true value. The other possible source of error is brought to one's notice by the fact that Joule and Thomson make no mention of having applied a stem correction to the readings of the thermometer which measured the temperature of the large water bath. This bath temperature was assumed by them (correctly, since in their apparatus the large copper tube in the bath was 60 feet long and 2 inches in diameter) to be the temperature of the gas as it entered the porous plug. But the thermometer, which measured the bath temperature, was so placed that its bulb was near the nozzle and in the observations at high temperatures must have had a considerable length of its stem and of mercury thread exposed to air at a temperature far below that of the bath. The thermometer would have read too low and, if no stem corrections were applied, the observed thermal effect would have been too small. None of the discrepancies between their results and mine is too large to be accounted for by reasonable assumptions as to the magnitude of these two possible errors in their observations.

In addition to the acknowledgments in the introduction of this paper I wish to acknowledge my hearty thanks to Dr. S. R. Cook, Mr. C. W. Waggoner, Mr. L. Howe and especially to Mr. H. J. Lathrop for help in taking observations during the work of this year.

In a later paper I shall show that it is possible to separate the thermal effects, measured in this research, into the two essential parts, one due to the external work which is done by the gas, the other — the pure Joule effect — due to the work done against the forces of intermolecular attraction; for this separation the available data on the compressibility of CO_2 will be used. The theoretical treatment of the results — their bearing upon the various characteristic gas equations, the possible development of such an equation for this gas, the deduction of a law of molecular attraction — will also be given in that paper.

SUMMARY.

The porous plug form of apparatus was used in this piece of work. The difference between the pressures on the two sides of the plug was about 1 atm. for all of the determinations. The differences in temperatures, (1) of the gas before and after passing through the plug, (2) of the gas and of the large water bath, which surrounded the copper heating (or cooling) tube, were measured by thermo-electric junctions; the thermo-electro-motive forces were measured by a modified potentiometer method.

In order to obtain the magnitude of the cooling effect for pure CO_2, determinations were made at a given temperature and at a given pressure with gas containing various percentages of impurity and these results were then extrapolated for pure CO_2. At 0° C. the results of such extrapolation show no dependence of the thermal effect upon pressure until a pressure of 26.4 atm. is reached; the one result obtained here indicates an increase over the values observed at lower pressures. At 20° C. the thermal effect

is independent of pressure as far as observations were carried; 41 atm. was the highest pressure reached at this temperature. The dependence of the cooling effect upon temperature is shown by the full line of Fig. 7; for purposes of comparison the results of the Joule-Thomson determinations for CO_2 are also represented in this figure, by the dotted line.

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ON THE APPLICATION OF SPECTRAL BANDS IN DETERMINING ANOMALOUS DISPERSION AND ACHROMATIC SYSTEMS OF VARIOUS TYPES.

By D. B. Brace.

IF two systems of interfering rays, after undergoing different phase-changes, in whatever way, are examined spectrally, dark bands are found for those frequencies where destructive interference occurs. If two sets be examined in juxtaposition, they may be made to coincide, either throughout the entire range of the spectrum, or only over certain portions. The former indicates perfect, the latter partial, differential achromatism. In general, the first is unrealizable; but the latter may be attained to a greater or less extent, particularly in the visible spectrum, by means of certain elements which constitute, in special combinations, achromatic systems.

If N represents the number of times destructive interference, by whatever mode, occurs for such a system, in varying the wave-length from $\lambda = \lambda_{\infty}$ to $\lambda = \lambda_D$, say, then $[\partial N/\partial \lambda]\delta\lambda$ represents the number of bands in the spectrum between wave-lengths λ and $\lambda + \delta\lambda$. If, by any change, we can make this number the same for a second element, we should have

$$\frac{\partial N'}{\partial \lambda} = \frac{\partial N''}{\partial \lambda}. \qquad (1)$$

The pair is then said to be differentially achromatic for these two wave-lengths. If the bands coincide between these limits, this couple is perfectly achromatic within this region. In the former, residual spectral effects occur which produce chromatism to a greater or less degree, which latter also occurs outside these limits.

If we integrate (1), we have

$$N' = N'' + k. \tag{2}$$

This shows that if we should vary λ in each element from λ_∞ to λ_D say, whère achromatism occurs, and count the number of times destructive interference occurs; or if we should begin in the spectrum at λ_∞ and count the bands up to λ_D, we should, in general, find a different number or order for each element of the pair.

N may be readily obtained if we can vary it in any way as I have already shown.[1] Thus if N_∞, N_D, and N_x represent the orders for λ_∞, λ_D, and λ_x respectively, and N_∞', N_D', and N_x' the orders obtained after any variation, we shall have:

$$N_D - N_\infty = N_D \qquad N_D' - N_\infty' = N_D'$$
$$N_x - N_\infty = N_x \qquad N_x' - N_\infty' = N_x'$$

or

$$N_x - N_D = p$$

and

$$N'_x - N_D' = np,$$

if $N_\infty' = N_\infty$ and p is the number of bands between the two wave-lengths λ_D and λ_x, and np the number when N is changed to N'.

We also have

$$N_D' - N_D = m$$

and

$$\frac{N_x' - N_D'}{N_x - N_D} = n = \frac{N_D'}{N_D} = \frac{N_x'}{N_x},$$

since

$$\frac{N_D' - N_\infty'}{N_D - N_\infty} = \frac{N_D'}{N_D},$$

if

$$N_\infty = N_\infty' = 0$$

where m is the number of bands passing λ_D in the positive direction, toward the red, say, in changing N_D to N_D'.

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[1] Phil. Mag., Oct., 1899, p. 345; also Rendtorff, Phil. Mag., May, 1901, p. 539, and Williams, Phys. Rev., April, 1904, p. 280.

Hence,

$$N_D = \frac{m}{n-1}. \qquad (3)$$

If for λ_∞, $N_\infty \neq 0$, or $= \varphi$, say, then (3) holds only for the corresponding portion or phase φ of the bands. Thus if $\varphi = \lambda/2$, we must use the white bands instead of the black bands in the settings and the countings to obtain N. The true order will then be $N + \varphi$. We have thus the methods at hand of determining the degree of achromatism and also the orders which must be used to reduce the chromatism to a minimum. A similar method will give the order of the same space without the medium, or we may find the thickness by determining the number of air-bands N_{E-D} between two wave-lengths λ_D and λ_E, say. We shall then have at once the data from which we can find the thickness. Thus, if

$$\mu_0 = 1,\ \frac{d}{\lambda_E} - \frac{d}{\lambda_D} = N_{E-D} \text{ or } d = N_{E-D}\left(\frac{\lambda_D \lambda_E}{\lambda_D - \lambda_E}\right).$$

We have thus the absolute index needed in the technical applications of these principles, which will be embodied in the usual formulæ after transformation from the above equations.

ANOMALOUS DISPERSION.

In this case we have to deal with relative phase-retardations of the two interfering systems due to a difference in path, neglecting for the moment phase-changes at the bounding surface.

If d is the thickness and μ the index of the medium,

$$N = \frac{d\mu}{\lambda};\ \text{and } N_0 = \frac{d_0\mu_0}{\lambda} \qquad (4)$$

for the same space with a medium of constant index μ_0.

Thus

$$\frac{\partial N}{-\partial \lambda} = \frac{d}{\lambda^2}\left(\mu + \lambda \frac{\partial \mu}{-\partial \lambda}\right) \text{ and } \frac{\partial N_0}{-\partial \lambda} = \frac{d_0\mu_0}{\lambda^2}. \qquad (5)$$

If we should be able to adjust the two sets of bands to coincidence at any point of the spectrum, we should have from (1)

$$\frac{\partial N}{-\partial \lambda} = \frac{\partial N_0}{-\partial \lambda}.$$

Hence,

$$\frac{d\mu}{\lambda}+\frac{\partial(d\mu)}{-\partial\lambda}=\frac{d_0\mu_0}{\lambda}\text{ or }\frac{d\mu}{\lambda}-\frac{d_0\mu_0}{\lambda}=-\frac{\partial(d\mu)}{-\partial\lambda}=k=N-N_0. \tag{6}$$

Since, if there is a coincidence between the bands with constant index and those of the medium to be examined, k must be a whole number, we shall have

$$\frac{\partial(d\mu)}{-\partial\lambda}=0, \tag{7}$$

if $N=N_0$. Thus, if by trial we can obtain a set of coincidences and then find, by the method of counting given above, that the orders are the same, μ must be constant in this region and hence be a maximum or a minimum, or have a point of inflection ; that is, the tangent to the curve of dispersion is parallel to the coördinate axis of λ. For example, taking $\mu_0=1$, as in the case of a vacuum (or of air, approximately), let us compare the air-bands with those of fuchsin, say. In the curve of dispersion of the latter, Fig. 1, as determined by Cartmel,[1] equation (7) holds at b and d on curve I. and the order N_1 of the air bands is the same as N_2 that of fuchsin at b ; and N_1' and N_2' are the same at d. Curve II. may illustrate a reduction in the anomaly, in a solution, say, and Curve III. a still further reduction, the points of maximum and minimum coinciding

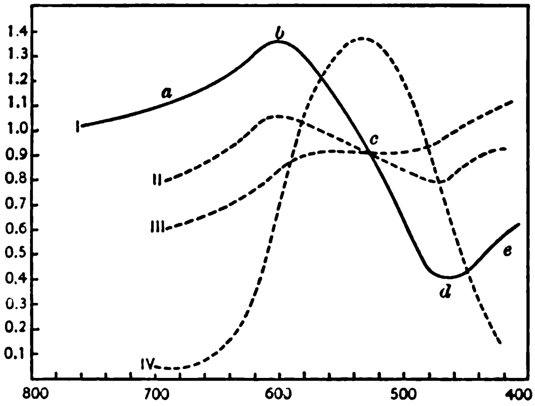

Fig. 1.

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[1] Phil. Mag., Aug., 1903, p. 213.

at a point of inflection c. At each of these points a characteristic distribution of the bands occurs from which we can readily interpret the nature of the anomaly. Referring to (5) again, since at these points

$$\frac{d\mu}{\lambda^2} = \frac{d_0\mu_0}{\lambda^2},$$

we have the residual term $d/\lambda\ \partial\mu/-\partial\lambda$ from which to determine the character of the curve at these points.

Thus $\partial\mu/-\partial\lambda$ is + going from a to b and − going from b to c, or

$$\frac{\partial N}{-\partial\lambda} > \frac{\partial N_0}{-\partial\lambda}$$

and

$$\frac{\partial N}{-\partial\lambda} < \frac{\partial N_0}{-\partial\lambda},$$

respectively; *i. e.*, on the red side of a coincidence, the bands crowd together; while, on the violet side, they spread out relatively to the air-bands in case of a maximum. Going from c to d $\partial\mu/-\partial\lambda$ is − and from d to e it is +, or

$$\frac{\partial N}{-\partial\lambda} < \frac{\partial N_0}{-\partial\lambda}$$

and

$$\frac{\partial N}{-\partial\lambda} > \frac{\partial N_0}{-\partial\lambda},$$

respectively, *i. e.*, if, on the red side of a coincidence, the bands of the medium spread out and on the violet side they crowd together more than the air-bands of the same order, the region has a minimum index. On Curve III., at a point of inflexion c, $\partial\mu/-\partial\lambda$ is + on the red and + on the violet side, or

$$\frac{\partial N}{-\partial\lambda} > \frac{\partial N_0}{-\partial\lambda}$$

in each case; *i. e.*, if the bands shorten with respect to the air bands of the same order on each side of a coincidence, the index has a point of inflexion.

In the region beyond a, since the bands must begin to coincide again before $\lambda = \lambda_\infty$, they must begin to lengthen relatively to the air-bands so as to coincide again at $\lambda = \lambda_\infty$. These various characteristics are illustrated in Fig. 2.

This apparent crowding together and spreading out of the bands is the more marked, the more pronounced the anomaly, being more marked in band- and line-spectra.

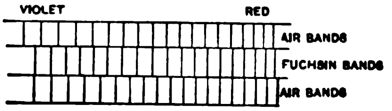

Fig. 2.

If the index of the medium of comparison is not constant, as it is in the case of a vacuum (or air) but varies slowly and uniformly, we can still apply similar tests for any anomalies which may exist. Thus from

$$\frac{\partial N}{-\partial\lambda} = \frac{\partial N_0}{-\partial\lambda}$$

we should have, in such a case,

$$\frac{d\mu}{\lambda} + \frac{\partial(d\mu)}{-\partial\lambda} = \frac{d_0\mu_0}{\lambda} + \frac{\partial(d_0\mu_0)}{-\partial\lambda}$$

or

$$\frac{\partial(d\mu)}{-\partial\lambda} = \frac{(d_0\mu_0)}{-\partial\lambda}, \text{ if } N = N_0,$$

and

$$\frac{\partial\mu}{-\partial\lambda} = \frac{d_0}{d}\,\frac{\partial\mu_0}{-\partial\lambda}. \tag{8}$$

Since d_0/d will not be large (rarely, if ever, equal to 2 for liquids and solids) and as the inclination of the dispersion curve to the λ-axis is always small for frequencies which are not near the natural frequencies of the medium, $\partial\mu/\partial\lambda$ will be small; and the crowding and spreading of the bands should occur approximately at a maximum or a minimum point, just as in a case when air is used as a means of comparison. For a point of inflection, the test might indicate a close maximum-minimum region. Thus, water (as a solvent), glass, mica, etc., could be used in detecting anomalous dispersion, or a definite number of air-bands may be added.

If, instead of there being a single medium in the path of each of the systems of interfering rays, there are several, in addition to the anomalous medium to be examined, similar considerations will show that the criteria for the anomalies are the same.

Let the resultant orders for the two sets of bands which are to be compared be represented by N' and N'' where $N' = N + N_1' + N_2' + \cdots N_m'$ and $N'' = N_0 + N_1'' + N_2'' + \cdots N_m''$.

Then if

$$\frac{\partial N'}{\partial \lambda} = \frac{\partial N''}{\partial \lambda},$$

we have

$$\frac{\partial N}{\partial \lambda} - \frac{\partial N_0}{\partial \lambda} + \frac{\partial N_1'}{\partial \lambda} - \frac{\partial N_1''}{\partial \lambda} + \cdots \frac{\partial N_m'}{\partial \lambda} - \frac{\partial N_m''}{\partial \lambda} = 0.$$

When the orders of the two sets of interfering bands are made the same before inserting the media to be compared, as can readily be realized in various interfering systems by suitable experimental conditions, we shall have

$$N_1' = N_1'', N_2' = N_2'' \cdots N_m' = N_m''$$

and hence

$$\frac{\partial N}{\partial \lambda} = \frac{\partial N_0}{\partial \lambda} \qquad (9)$$

Thus the crowding and spreading of the resultant bands will indicate the presence of anomalies as before. The additional bands then serve as lines of reference for making measurements, when the orders of the media to be compared are too low to give sufficient bands to make consecutive comparisons throughout the spectrum. The equality $N = N_0$, however, cannot be determined from (3) so readily as before by the process of counting. Either the additional bands must be excluded in order to use (3) as usual, or the bands from these media must be counted when they are introduced into the field from zero order up to the orders to be used. For low orders, less than unity, the latter method is usually preferable. With the previous method we may determine whether we have a true zero order by inserting a compensating element of the order m, say for the D-line. The dispersion of this compensating element must be the same as that of the medium producing the bands. If then we do not find the final band on the D-line, the interfering system may be adjusted until we get coincidence of the order with the D-line. We may then proceed in the usual way, by counting, to obtain the order of the unknown element, noting, however, any change from the zero order of the interfering system and adjusting, accordingly, if necessary. Should there be any uncertainty as to the proper compensation for other parts of the spectrum, we should note whether the other bands are in their proper places in the rest of the spectrum also. The various characteristics discussed above may be readily represented graphically. From equations (4) we have

$$N\lambda = d\mu, \tag{4a}$$

and

$$N_0\lambda = d_0\mu_0 h, \tag{4b}$$

where μ is a constant. (4*b*) represents a series of equilateral hyperbolæ, with different parameters depending on $d_0\mu_0$ being taken as unity. In Fig. 3 the curve *A B C D E* is plotted from Cartmel's data. The full lines represent the rectangular hyperbolæ, while dotted lines represent the deviations from the corresponding hyperbolæ, when μ_0 varies but slowly, as it does considerably beyond the anomalous region. The curve *A B C D E* represents the variations in N due to the fluctuations of μ in its anomalous region. Thus from

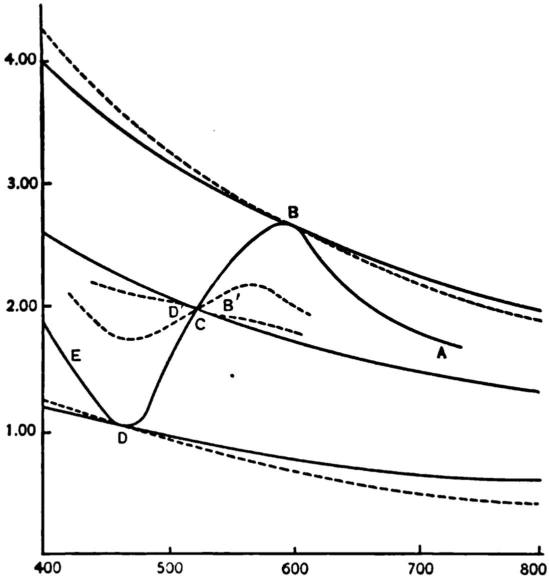

Fig. 3.

A to *B*, N increases more rapidly than N_0, from *B* to *D* more slowly, then more rapidly from *D* to *E*. Beyond *A*, N increases less rapidly than N_0, becoming finally asymptotic to the axis of λ at $\lambda = \lambda_\infty$, while beyond *E*, N increases less rapidly, becoming asymptotic to the axis of N at $\lambda = \lambda_0$ where μ becomes unity. In the case of an inflexion, the curve $B'CD'$ becomes tangent on crossing the hyperbola *C*. Thus the order N increases more rapidly before and after crossing the hyperbola, but diminishes more rapidly beyond B' and D'.

Fig. 2 is a reproduction of Cartmel's fuchsin-bands, showing the fluctuations in width referred to. Toward the violet end, we see the fuchsin-bands are relatively narrower, while they are wider than the air-bands in the central portion, indicating a minimum in this region. At the red end the fuchsin-bands are narrower than the air-bands, thus indicating a maximum region.

The method of interferences in the study of dispersion has much to recommend it over the usual prismatic methods. The strong absorption in the anomalous region prevents the use of any but the smallest angled prism, which involves serious instrumental errors. The spectral interference methods referred to eliminate these errors, since the factors sought can be determined by a process of counting and are hence independent of the angle of the film, which may vary in any arbitrary way so long as the change in thickness is not so abrupt as to prevent the "count" of the bands. Media through which it would be impossible to obtain sufficient light for measurements, if in prismatic form, can readily be examined in thin films in this way.

The use of spectral bands presents us with a method which unfolds before the eye, in the position of the bands in the spectrum, an exact record of whatever the medium has impressed upon the various trains of waves which have passed through it. Using the criteria mentioned above, we may at once locate the presence of any dispersive characteristic in the spectrum which the medium may possess. Thus, if in addition a quantitative determination is to be made, we may localize our measurements to this particular region.

The special method of interference to be adopted will depend partly on the nature of the media studied. When the films are thick enough and also sufficiently transparent to give the characteristic interference bands by reflection, when examined directly by the spectroscope, observations are simplified. Comparison can be conveniently obtained by means of a double rectangular collimator one half the field of which is illuminated with light from one of its slits directly, and the other half with light from the other slit after total reflection from a rectangular prism placed before the objective similar to the arrangement used by the writer[1] and later by Rendtorff,[2] in the study of differential double refraction. In this case, total reflecting prisms may be placed at the slits to throw the light upon the films and thence into the collimator, as used by Cartmel[3] in finding the thickness of his films. Instead of the above arrangement, two collimators may be arranged with the compound prism as used in the spectrophotometer of the writer.[4] These arrangements allow of independent movements of each of the two media under examination, and facilitate the adjustments considerably over those made when the two films are placed in juxtaposition before the same slit. The former arrangement also brings the two sets of bands closer together. If the absorption is great, the film to be examined may be placed between semi-transparent mirror-surfaces to equalize the intensities of the two interfering beams. If the order is too low to give sufficient bands for comparison, an auxiliary film may be introduced in series with the film to be examined and the method of comparison of mixed bands described above be used. Under the latter conditions, we may also use an interferometer, preferably of such a type that the light may pass through the film once only. The method adopted by the writer, of converging the light within an interferometer similar in type to that of Jamin and of using a mixed system of bands, should be chosen. Cartmel[5] has used this arrangement most effectively in his studies on the dispersion of fuchsin. Here again we have the spectral bands after passing the interferometer. This spectral analysis of interferential phenomena has much to recommend it over the customary mode of analyzing the light first and examining afterward, with homogeneous rays, these interference effects.

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[1] L. c.

[2] L. c.

[3] L. c.

[4] Phil. Mag., Nov., 1899, p. 420; Astrophys. Journ., Jan., 1900.

[5] L. c.

When very slight anomalies are present and the absorption is small, we should resort to high orders and the high resolving power of the grating. Thus, in the examination of weak solutions of varying concentrations of anomalous substances, the growth of the anomaly is at once made evident. Here, several thousand bands may be introduced into the spectrum, and, as the effect is cumulative, any slight relative shift in the bands becomes at once evident. Comparison bands, from the solvent say, may be introduced by means of a second slit arranged in duplication of the system used by Williams[1] in determining refractive indices, the Frauenhofer lines being used for reference along with the bands themselves. In fact, for the study of anomalies in gases, this arrangement should be used on account of the high resolving power required.

ROTARY POLARIZATION.

As is well known, if a rotary medium be placed between two nicol prisms and the light transmitted through this system be examined spectrally, dark bands will appear for those wave-lengths the principal planes of whose vibrations are at right angles to that of the analyzing nicol. This extinction will recur for every increment or decrement in the rotation of 180°. Thus the order of the bands will be proportional to the rotation, or

$$\frac{\partial N}{-\partial\lambda} \propto \frac{\partial\rho}{-\partial\lambda}.$$

Hence if

$$\frac{\partial N}{-\partial\lambda} = \frac{\partial N_0}{-\partial\lambda},$$

$$\frac{\partial\rho}{-\partial\lambda} = \frac{\partial\rho_0}{-\partial\lambda}$$

and

$$\rho = \rho_0 + \text{const.} \tag{10}$$

is the condition for achromatism of such a couple. The total rotation may be obtained by the process of counting, as described above, to obtain the order, the thickness of the rotary medium being varied. Thus, taking black bands as our basis of calculation, the nicols must be crossed. Since here our order corresponds to a rotation equal to 180°, we have from (3)

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[1] L. c.

$$N_D 180^\circ = \rho_D = \frac{m}{n-1} 180^\circ. \tag{11}$$

The application of this spectral method to achromatic comparisons is practically limited to a very few substances on account of the great rotations necessary to produce sufficient bands.

Thus, quartz would give only about 9 or 10 bands in the visible spectrum for a thickness of 50 mm. As quartz has a much higher rotary power than most active substances, very considerable lengths of the media would be necessary in any comparisons. The same is true of magnetically active media. For this same reason the above tests for anomalous rotary dispersion are impracticable except with mixed systems, using perhaps quartz to give sufficient bands for comparison. Exact quantitative comparison should of course be made by means of half-shade plane polarizing systems. The importance of achromatism to saccharimetry warrants, perhaps, such spectral comparisons, to determine the region in the spectrum giving the best rotary achromatism with quartz; or, in fact to determine a more perfectly achromatizing comparator than quartz itself.

DOUBLE DIFFERENTIAL REFRACTION.

The relative retardation produced by a double-refracting plate placed between two nicols, may also be examined by means of a spectroscope. Thus, if the nicols are crossed and the principal axis of the plate makes an angle of 45° with that of the polarizing system, the light transmitted by such a plate will be cut out when the difference in phase between the two components, expressed in wavelengths, is a whole number. As this difference is a function of the frequency, we should obtain the well known bands in the spectrum corresponding to those frequencies. I have already used the above method[1] of determining the orders of individual plates and have also determined the particular orders to be used in crossed achromatic couples. Rendtorff[2] has also made similar determinations using a grating. This method has revealed persistent errors in old determinations of the orders of plates arising from the assumption that, if

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[1] L. c.

[2] L. c.

$$\frac{\partial N'}{-\partial\lambda} = \frac{\partial N''}{-\partial\lambda},$$

we shall have $N' = N''$, which is seriously in error in the comparison of one crystal with another, as is customary with crystallographers. Thus, if

$$\frac{\partial N'}{-\partial\lambda} = \frac{\partial N''}{-\partial\lambda},$$

we should have

$$N' = N'' + \text{const.}$$

or

$$d'(\mu_e' - \mu_0') = d''(\mu_e'' - \mu_0'') + \text{const.} \qquad (12)$$

where

$$N' = \frac{d'(\mu_e' - \mu_0')}{\lambda} \text{ and } N'' = d''\frac{(\mu_e'' - \mu_0'')}{\lambda}$$

and μ_e and μ_0 are the two principal indices.

Mouton[1] claimed to have obtained anomalous differential dispersion in selenite. An examination of Rendtorff's bands by means of the maximum-minimum criteria, shows no such fluctuations. That such anomalies are present in other regions may be expected, since the natural frequencies of the two rectangular components are usually different, as exists in the case of tourmaline, Iceland Spar, etc. That such bands may be tested by our criteria is evident from the factors constituting N, which is evidently a mixed system and, hence, conformable to our rules, being a difference instead of a summation system, the one having a slow variation in the dispersion since it is not near its natural frequency. Hence our comparison bands may be bands from thin films, or they may be differential bands from another crystal having no anomaly in this region. The applications of this method in the case of crystals, as well as the experimental arrangements for making the comparisons, may be found in the papers already referred to.

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[1] Wien, Ak. Ber., XXXVI. (2), p. 793, 1877.

Acromatic Compensation and Interference.

In many of the determinations of the velocities of systems of waves in different media, white light is used in an interferometer and the measurements are made to depend upon the position of the so-called "central" or white band. When a zero method is adopted, an optical compensation is used to bring back this "central" band to the fiducial line. If this is not done the apparent displacement of this band is usually measured directly. Either of these methods may introduce serious errors in the results. Considerations, similar to those mentioned above as to the achromatism of the two systems of interfering rays, will enable us to determine when such errors do enter, and their proper corrections. In the "zero" method, the compensation is produced either by an adjustment of one of the surface elements of the interferometer or by the introduction of an additional amount of a retarding medium. An example of the former practice is shown in the Michelson type and of the latter in the Jamin type of inteferometer. It is evident that both the zero and the displacement methods involve essentially the same chromatic differentiation, since in both we have the introduction of like compensating components. We may therefore discuss them under the same head. Such systems are mixed systems the consideration of which may be reduced to that of two elements, namely, the one to be examined and the other the compensating factor. The compensating medium is thus either a vacuum (or air) or a solid (like glass, mica, etc.) or a liquid (such as the solvent in a solution, etc.). Referring to equations (9), we have now, as the condition of a white band, our equation of reference

$$\frac{\partial N}{-\partial\lambda} = \frac{\partial N_0}{-\partial\lambda}$$

or

$$N = N_0 + k.$$

Thus our so-called white band will be achromatic to a greater or less degree, depending on the extent of the region over which the first equality holds. If then sN_D is the order of the compensating elements $s(N_0+k)_D$ must be the order of effect introduced by the unknown element. The constant k should be determined beforehand under the same conditions of luminosity, absorption, etc., as those of the compensation. Thus, if the silicate crown glass strips, usually mounted in connection with Jamin's interferometer, were to be used to compensate displacements due to borate flint specimens, errors would enter in, since, in this case, $k \neq 0$. Similar errors would occur in comparing the solution of certain substances with the solvent itself. When the compensation consists of a displacement of one of the surface elements, the compensating medium is usually air (where of course the paths are so small that dispersion does not enter), and we should not have an achromatic band, unless a region of inflection of the refractive index of the medium existed over the most luminous part of the spectrum used, so as to give a nearly constant index. If this condition did not obtain, the so-called central band would be imperfectly achromatized. Stokes[1] has already called attention to the error in the latter instance in determining refractive indices by the displacement of the bands. This phenomena, referred to by Stokes, is, however, accompanied by a certain amount of chromatism of the band, and for this reason the error is readily detected. In the examples mentioned above this error cannot be thus detected. Our only resource is the use of spectral bands, if a preliminary examination of the two elements is not made beforehand. Mention may again be made of the convenience of this system on account of our ability to determine the order by the method of counting. Thus, if we are determining the index (and dispersion) of a gas, it is quite unnecessary to count the total number of bands, on the introduction of the gas into the path of one of the interfering rays. We only need to vary the quantity by a slight amount, in order to get the number of passages m of the bands at any point in the spectrum and note the ratio of n. The same would hold in the case of solids, solutions, etc. The tediousness of many of the old measurements could thus be greatly reduced.

Attention might also be called to the test for anomalies, in such measurements on gases, which would occur near the region of absorption.

The fact that we may have achromatism without the orders being the same, *i. e.*, $k \neq 0$, if

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[1] Math. and Phys. Papers, Vol. II., p. 361.

$$\frac{\partial N}{-\partial\lambda}=\frac{\partial N_0}{-\partial\lambda},$$

shows that in the experiments on so-called Talbot's bands we should not obtain them, even when the retardation is introduced in the appropriate way.

Achromatic Refracting Systems.

We may extend to achromatic systems a treatment[1] similar to that which I have already given, in discussing the variation in direction which is produced by any arbitrary system of reflecting and refracting surfaces upon a ray which has been subjected to a change in its velocity or in the phase of its vibration. Consider the refraction of paraxial rays, N' and N'', at a series of surfaces, s_1, $s_2 \cdots s_m$, very near together. The order of the undeviated ray is $N' = N_0' + N_1' + N_2' + \cdots + N_m'$, and that of a ray at a distance δs from the axis is

$$N'' = N_0'' + N_1'' + N_2'' + \cdots + N_m'' = N_0' + N_1' + N_2' + \cdots N_m' + \frac{\partial N_0'}{\partial s}\delta s + \frac{\partial N_1'}{\partial s}\delta s + \frac{\partial N_2'}{\partial s}\delta s + \cdots + \frac{\partial N_m'}{\partial s}\delta s. \tag{13}$$

In all cases of refraction at a surface, destructive interference must occur at all points in space, corresponding to this interval, beyond the surfaces, except at a point on the undeviated ray which is designated as the focus of the system of rays. All disturbances must therefore arrive in the same phase at this point. Hence

$$N' = N''$$

or

$$\frac{\partial N}{\partial s} = \frac{\partial}{\partial s}(N_0 + N_1 + N_2 + \cdots N_m) = 0. \tag{14}$$

This corresponds to the condition of zero spherical aberration.

The order of the axial ray for some other wave-length, $\lambda + \delta\lambda$, is

$$N' = N_0' + \frac{\partial N_0'}{\partial\lambda}\delta\lambda + N_1' + \frac{\partial N_1'}{\partial\lambda}\delta\lambda + N_2' + \frac{\partial N_2'}{\partial\lambda}\delta\lambda + \cdots N_m' + \frac{\partial N_m'}{\partial\lambda}\delta\lambda$$

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[1] Phil. Mag., Apr., 1901, p. 464.

and for a ray of the same wave-length at distance δs is

$$N'' = N_0'' + \frac{\partial N_0''}{\partial \lambda}\delta\lambda + N_1'' + \frac{\partial N_1''}{\partial \lambda}\delta\lambda + N_2'' + \frac{\partial N_2''}{\partial \lambda}\delta\lambda + \cdots N_m''$$

$$+ \frac{\partial N_m''}{\partial \lambda}\delta\lambda = N_0' + \frac{\partial N_0'}{\partial s}\delta s + \frac{\partial N_0'}{\partial \lambda}\delta\lambda + \frac{\partial^2 N_0'}{\partial\lambda\partial s}\delta\lambda\delta s$$

$$+ N_1' + \frac{\partial N_1'}{\partial s}\delta s + \frac{\partial N_1'}{\partial \lambda}\delta\lambda + \frac{\partial^2 N_1'}{\partial\lambda\partial s}\delta\lambda\delta s +$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$+ N_m' + \frac{\partial N_m'}{\partial s}\delta s + \frac{\partial N_m'}{\partial \lambda}\delta\lambda + \frac{\partial^2 N_m}{\partial\lambda\partial s}\delta\lambda\delta s.$$

As $N' = N''$ for every wave-length, we must have as before

$$\frac{\partial N}{\partial s} = 0$$

and also

$$\frac{\partial^2 N}{\partial\lambda\partial s} = 0 \quad \text{or} \quad \frac{\partial N}{\partial \lambda} = \text{const.} \tag{15}$$

We shall now transform these equations so as to embody the factors of index, curvature, etc., used in the ordinary treatment of refracting surfaces. Let there be a single refracting surface s_1, Fig. 4, whose radius of curvature is r_1.

Since

$$N = \frac{\mu l}{\lambda},$$

we have

$$\frac{\partial N_0}{\partial s} = \frac{\mu_0}{\lambda}\frac{\partial l_0}{\partial s}. \tag{16}$$

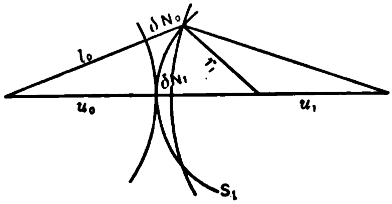

Fig. 4.

By geometry we have also

$$\frac{\partial l}{\partial s} = \frac{\delta s}{2r}. \tag{17}$$

Since we are dealing with paraxial systems in which we neglect second-order small quantities, if we put $\delta s = 2$, we have

$$[illegible] \qquad (18)$$

shows that in the experiment [illegible] radiant to the surface s_1 not obtain them, even wh[illegible]

$$[illegible]\left(\frac{1}{u_0}-\frac{1}{r_1}\right). \qquad (19)$$

appropriate way.

Achrom[illegible] from s_1 to the image of the radiant,

We may extend to ac[illegible] that which I have alre[illegible]

$$[illegible]\left(\frac{1}{r_1}-\frac{1}{u_1}\right). \qquad (20)$$

tion which is produ[illegible] refracting surfaces [illegible]

$$[illegible](N_0+N_1)=0$$

change in its velocit[illegible] refraction of parax[illegible] (20), we have $s_2 \cdots s_m$, very nea[illegible] $N' = N_0' + N_1'$ [illegible]

$$[illegible]=0 \quad \text{or} \quad \frac{\mu_1}{u_1}-\frac{\mu_0}{u_0}=\frac{\mu_1-\mu_0}{r_1}. \qquad (21)$$

∂s from the axis [illegible]

$N'' = N_0'' +$ [illegible] we have

$$+\cdots N[illegible] \qquad [illegible]-\frac{1}{u_0}=\frac{\mu_1-1}{r_1}. \qquad (22)$$

In all cas[illegible] medium, bounded by two surfaces s_1 and s_2, must occur [illegible] we have similarly beyond the [illegible] is designat[illegible] must then [illegible]

$$\frac{\partial N_0}{\partial s}=\frac{\mu_0}{\lambda}\left(\frac{1}{u_0}-\frac{1}{r_1}\right) \qquad (19)$$

or

$$\frac{\partial N_1}{\partial s}=\frac{\mu_1}{\lambda}\left(\frac{1}{r_1}-\frac{1}{r_2}\right) \qquad (20)$$

$$\frac{\partial N_2}{\partial s}=\frac{\mu_2}{\lambda}\left(\frac{1}{r_2}-\frac{1}{u_2}\right). \qquad (23)$$

This [illegible]

Th[illegible]

$$N' [illegible](N_0+N_1+N_2)=0=\frac{\mu_0}{\lambda}\left(\frac{1}{u_0}-\frac{1}{r_1}\right) + \frac{\mu_1}{\lambda}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)+\frac{\mu_2}{\lambda}\left(\frac{1}{r_2}-\frac{1}{u_2}\right)=0. \qquad (24)$$

[illegible] we have finally

$$\frac{1}{f_1}=\frac{1}{u_2}-\frac{1}{u_0}=\left(\frac{\mu_1}{\mu_0}-1\right)\left(\frac{1}{r_1}-\frac{1}{r_2}\right)$$

or, if $\mu_0 = 1$ (25)

$$\frac{1}{f_1}=\frac{1}{u_2}-\frac{1}{u_0}=(\mu_1-1)\left(\frac{1}{r_1}-\frac{1}{r_2}\right).$$

Consider now two lenses in contact; equation (15) gives us the condition for achromatism for the two wave-lengths λ and $\lambda+\delta\lambda$. We must therefore substitute in (15) the values of $\partial N/\partial s$ given in (19), (20) and (23), and differentiate with respect to λ. Thus for the first lens,

$$\frac{\partial}{\partial\lambda}\left(\frac{\partial N_0}{\partial s}\right)=\frac{1}{\lambda}\left(\frac{1}{u_0}-\frac{1}{r_1}\right)\frac{\partial\mu_0}{\partial\lambda}-\frac{\mu_0}{\lambda^2}\left(\frac{1}{u_0}-\frac{1}{r_1}\right) \tag{26}$$

$$\frac{\partial}{\partial\lambda}\left(\frac{\partial N_1}{\partial s}\right)=\frac{1}{\lambda}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda}-\frac{\mu_1}{\lambda^2}\left(\frac{1}{r_1}-\frac{1}{r_2}\right) \tag{27}$$

$$\frac{\partial}{\partial\lambda}\left(\frac{\partial N_2}{\partial s}\right)=\frac{1}{\lambda}\left(\frac{1}{r_2}-\frac{1}{u_2}\right)\frac{\partial\mu_2}{\partial\lambda}-\frac{\mu_2}{\lambda^2}\left(\frac{1}{r_2}-\frac{1}{u_2}\right). \tag{28}$$

For the second lens,

$$\frac{\partial}{\partial\lambda}\left(\frac{\partial N_2}{\partial s}\right)=\frac{1}{\lambda}\left(\frac{1}{u_2}-\frac{1}{r_3}\right)\frac{\partial\mu_2}{\partial\lambda}-\frac{\mu_2}{\lambda^2}\left(\frac{1}{u_2}-\frac{1}{r_3}\right) \tag{29}$$

$$\frac{\partial}{\partial\lambda}\left(\frac{\partial N_3}{\partial s}\right)=\frac{1}{\lambda}\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda}-\frac{\mu_3}{\lambda^2}\left(\frac{1}{r_3}-\frac{1}{r_4}\right) \tag{30}$$

$$\frac{\partial}{\partial\lambda}\left(\frac{\partial N_4}{\partial s}\right)=\frac{1}{\lambda}\left(\frac{1}{r_4}-\frac{1}{u_4}\right)\frac{\partial\mu_4}{\partial\lambda}-\frac{\mu_4}{\lambda^2}\left(\frac{1}{r_4}-\frac{1}{u_4}\right). \tag{31}$$

Making $\mu_0=\mu_2=\mu_4=1$ and substituting the above values in (15), we have

$$\begin{aligned}\frac{\partial^2 N}{\partial\lambda\partial s}=\frac{1}{\lambda_2}\Bigg\{&\lambda\left[\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda}\right]\\ &+\left[(\mu_1-1)\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+(\mu_3-1)\left(\frac{1}{r_4}-\frac{1}{r_3}\right)+\frac{1}{u_4}-\frac{1}{u_0}\right]\Bigg\}=0.\end{aligned} \tag{32}$$

From (24) and (25) we see that we must have

$$\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda}=0 \tag{33}$$

and

$$\frac{1}{u_4}-\frac{1}{u_0}=\frac{1}{f_1}+\frac{1}{f_3}=(\mu_1-1)\left(\frac{1}{r_1}-\frac{1}{r_2}\right)+(\mu_3-1)\left(\frac{1}{r_3}-\frac{1}{r_4}\right). \qquad (34)$$

Substituting

$$\left(\frac{1}{r_1}-\frac{1}{r_2}\right)=\frac{1}{f_1(\mu_1-1)}$$

in (33), we have also

$$\frac{1}{f_1(\mu_1-1)}\frac{\partial\mu_1}{\partial\lambda}+\frac{1}{f_3(\mu_3-1)}\frac{\partial\mu_3}{\partial\lambda}=0. \qquad (35)$$

From these equations we may calculate the values of $r_1 \cdots r_4$ which will unite the wave-lengths λ and $\lambda+\delta\lambda$ in the conjugate points u_0 and u_4 on the axis.

Substituting in (33) the value of the curvatures from (20), we have

$$\frac{\lambda}{\mu_1}\frac{\partial\mu_1}{\partial\lambda}\frac{\partial N_1}{\partial s}+\frac{\lambda}{{}_3}\frac{\partial\mu_3}{\partial\lambda}\frac{\partial N_3}{\partial s}=0. \qquad (36)$$

This shows that $\partial N_1/\partial s$ must be of opposite sign to $\partial N_3/\partial s$ for normal dispersion. Hence the variation in thickness of the one lens must be opposite to that of the other to obtain achromatism.

The value of $(\partial\mu_1/\partial\lambda)/(\partial\mu_3/\partial\lambda)$ from (33) may be readily obtained by means of spectral bands. We have from (5)

$$\begin{aligned}\frac{\partial N_0}{-\partial\lambda}&=\frac{d_0\mu_0}{\lambda^2}\\ \frac{\partial N_1}{-\partial\lambda}&=\frac{d_1\mu_1}{\lambda^2}+\frac{d_1}{\lambda}\frac{\partial\mu_1}{-\partial\lambda}\\ \frac{\partial N_3}{-\partial\lambda}&=\frac{d_3\mu_3}{\lambda^2}+\frac{d_3}{\lambda}\frac{\partial\mu_3}{-\partial\lambda}.\end{aligned} \qquad (37)$$

If we make $N_0=N_1=N_3$, we have

$$\frac{d_3}{d_1}\,\frac{\dfrac{\partial N_1}{-\partial\lambda}-\dfrac{\partial N_0}{-\partial\lambda}}{\dfrac{\partial N_3}{-\partial\lambda}-\dfrac{\partial N_0}{-\partial\lambda}}=\frac{\dfrac{\partial\mu_1}{-\partial\lambda}}{\dfrac{\partial\mu_3}{-\partial\lambda}}. \qquad (38)$$

Thus if we have air-bands in juxtaposition with the bands of the first medium, and then with those of the second medium, and adjust until they have the same order for one wave-length, λ_c, say, the ratio of the respective increments in order, over the air-bands for another wave-length, will be the ratio of the increments in indices sought.

In order that m wave-lengths may have a common focus, m lenses would be required, and we should find in a similar way the following $m - 1$ equations,

$$\left.\begin{array}{l}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda_1}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda_1}+\cdots+\left(\frac{1}{r_{2m-1}}-\frac{1}{r_{2m}}\right)\frac{\partial\mu_{2m-1}}{\partial\lambda_1}=0\\ \quad\vdots\qquad\vdots\qquad\qquad\vdots\qquad\qquad\qquad\vdots\qquad\qquad\vdots\\ \left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda_{m-1}}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda_{m-1}}+\cdots+\left(\frac{1}{r_{2m-1}}-\frac{1}{r_{2m}}\right)\frac{\partial\mu_{2m-1}}{\partial\lambda_{m-1}}=0\end{array}\right\} \quad (39)$$

or

$$\left.\begin{array}{l}\frac{1}{f_1(\mu_1-1)}\frac{\partial\mu_1}{\partial\lambda_1}+\frac{1}{f_3(\mu_3-1)}\frac{\partial\mu_3}{\partial\lambda_1}+\cdots+\frac{1}{f_{2m-1}(\mu_{2m-1}-1)}\frac{\partial\mu_{2m-1}}{\partial\lambda_1}=0\\ \quad\vdots\qquad\qquad\vdots\qquad\qquad\qquad\vdots\qquad\qquad\vdots\\ \frac{1}{f_1(\mu_1-1)}\frac{\partial\mu_1}{\partial\lambda_{m-1}}+\frac{1}{f_3(\mu_3-1)}\frac{\partial\mu_3}{\partial\lambda_{m-1}}+\cdots+\frac{1}{f_{2m-1}(\mu_{2m-1}-1)}\frac{\partial\mu_{2m-1}}{\partial\lambda_{m-1}}=0\end{array}\right\} \quad (40)$$

and the focal equation

$$\begin{aligned}\frac{1}{F}=\frac{1}{f_1}+\frac{1}{f_3}+\cdots+\frac{1}{f_{2m-1}}&=(\mu_1-1)\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\\ &+(\mu_3-1)\left(\frac{1}{r_3}-\frac{1}{r_4}\right)+\cdots+(\mu_{2m-1}-1)\left(\frac{1}{r_{2m-1}}-\frac{1}{r_{2m}}\right).\end{aligned} \quad (41)$$

Here $\partial\lambda_1, \partial\lambda_2, \cdots \partial\lambda_{m-1}$ are the increments in wave-lengths referred to some specified wave-length, λ_D, say; and $\partial\mu_1, \partial\mu_3 \cdots \partial\mu_{2m-1}$, the corresponding increments in index in each lens.

The above equations show that the order of sequence of the lenses is arbitrary. This method of satisfying the equation of achromatism (15), by achromatizing for different wave-lengths, gives rise to so-called secondary spectra.

We may, however, satisfy this equation of condition in a different way, which can now be realized, in part at least, experimentally, with less residual chromatism than the old method of using a greater number of lenses.

Instead of using m lenses of different indices, we may combine two having $m+1$ color coincidences. We shall then have the m equations,

$$\begin{aligned}
\frac{\partial^2 N}{\partial\lambda_1\partial s} &= \frac{\partial}{\partial\lambda_1}\left(\frac{\partial N_0}{\partial s}+\frac{\partial N_1}{\partial s}+\frac{\partial N_2}{\partial s}+\frac{\partial N_3}{\partial s}+\frac{\partial N_4}{\partial s}\right)=0 \\
\frac{\partial^2 N}{\partial\lambda_2\partial s} &= \frac{\partial}{\partial\lambda_2}\left(\frac{\partial N_0}{\partial s}+\frac{\partial N_1}{\partial s}+\frac{\partial N_2}{\partial s}+\frac{\partial N_3}{\partial s}+\frac{\partial N_4}{\partial s}\right)=0 \\
&\vdots \qquad\qquad\qquad \vdots \qquad\qquad\qquad \vdots \\
\frac{\partial^2 N}{\partial\lambda_m\partial s} &= \frac{\partial}{\partial\lambda_m}\left(\frac{\partial N_0}{\partial s}+\frac{\partial N_1}{\partial s}+\frac{\partial N_2}{\partial s}+\frac{\partial N_3}{\partial s}+\frac{\partial N_4}{\partial s}\right)=0
\end{aligned} \tag{42}$$

Proceeding in the same way as with (32), we should thus have the m equations

$$\begin{aligned}
\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda_1}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda_1}&=0 \\
\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda_2}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda_1}&=0 \\
\vdots \qquad\qquad\qquad \vdots \qquad\qquad &\vdots \\
\left(\frac{1}{r_1}-\frac{1}{r_2}\right)\frac{\partial\mu_1}{\partial\lambda_m}+\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\frac{\partial\mu_3}{\partial\lambda_m}&=0
\end{aligned} \tag{43}$$

and the focal equation

$$\frac{1}{f_1}+\frac{1}{f_3}=(\mu_1-1)\left(\frac{1}{r_1}-\frac{1}{r_2}\right)+\mu_3-1\left(\frac{1}{r_3}-\frac{1}{r_4}\right)\cdot \tag{34}$$

We have seen how, by means of (37) and (38), to achromatize for two wave-lengths by means of two lenses. We may by means of (43) achromatize for $m+1$ wave-lengths by means of *two* lenses. Suppose $m=2$, we have then to find the corresponding equations similar to (38) in terms of their orders. We have from (5)

$$\begin{aligned}
\frac{\partial N_0}{-\partial\lambda_1}&=\frac{d_0\mu_0}{\lambda^2} \\
\frac{\partial N_1}{-\partial\lambda_1}&=\frac{d_1\mu_1}{\lambda^2}+\frac{d_1}{\lambda}\frac{\partial\mu_1}{-\partial\lambda_1} \\
\frac{\partial N_1}{-\partial\lambda_2}&=\frac{d_1\mu_1}{\lambda^2}+\frac{d_1}{\lambda}\frac{\partial\mu_1}{-\partial\lambda_2}
\end{aligned} \tag{44}$$

$$\frac{\partial N_3}{-\partial\lambda_1} = \frac{d_3\mu_3}{\lambda^2} + \frac{d_3}{\lambda}\frac{\partial\mu_3}{-\partial\lambda_1}$$

$$\frac{\partial N_3}{-\partial\lambda_2} = \frac{d_3\mu_3}{\lambda^2} + \frac{d_3}{\lambda}\frac{\partial\mu_3}{-\partial\lambda_2}$$

where $\partial\lambda_1$ and $\partial\lambda_2$ are the increments in wave-length, referred to some wave-length of reference λ_D, of any two other wave-lengths, λ_C and λ_F, say.

If we make $N_0 = N_1 = N_3$, we shall have

$$\frac{\dfrac{\partial N_1}{-\partial\lambda_1} - \dfrac{\partial N_0}{-\partial\lambda_1}}{\dfrac{\partial N_1}{-\partial\lambda_2} - \dfrac{\partial N_0}{-\partial\lambda_2}} = \frac{\dfrac{\partial\mu_1}{-\partial\lambda_1}}{\dfrac{\partial\mu_1}{-\partial\lambda_2}} \tag{45}$$

$$\frac{\dfrac{\partial N_3}{-\partial\lambda_1} - \dfrac{\partial N_0}{-\partial\lambda_1}}{\dfrac{\partial N_3}{-\partial\lambda_2} - \dfrac{\partial N_0}{-\partial\lambda_2}} = \frac{\dfrac{\partial\mu_3}{-\partial\lambda_1}}{\dfrac{\partial\mu_3}{-\partial\lambda_2}}. \tag{46}$$

But (43) requires that

$$\frac{\dfrac{\partial\mu_1}{-\partial\lambda_1}}{\dfrac{\partial\mu_1}{-\partial\lambda_2}} = \frac{\dfrac{\partial\mu_3}{-\partial\lambda_1}}{\dfrac{\partial\mu_3}{-\partial\lambda_2}} \tag{47}$$

and hence we must have

$$\frac{\dfrac{\partial N_1}{-\partial\lambda_1} - \dfrac{\partial N_0}{-\partial\lambda_1}}{\dfrac{\partial N_3}{-\partial\lambda_1} - \dfrac{\partial N_0}{-\partial\lambda_1}} = \frac{\dfrac{\partial N_1}{-\partial\lambda_2} - \dfrac{\partial N_0}{-\partial\lambda_2}}{\dfrac{\partial N_3}{-\partial\lambda_2} - \dfrac{\partial N_0}{-\partial\lambda_2}}. \tag{48}$$

Equations (34) and (38) are the conditions for achromatism of two colors, while (48) is the further condition for achromatism of three colors by means of two lenses. Thus, suppose we have our three sets of spectral bands in the field of view, the air-bands being in the middle, we set for coincidence at the D-line say, making the sets of the same order, which can readily be accomplished by varying the thicknesses successively and counting the bands, as described above. The eye may then note the gain relatively to the air-bands of each of the other sets of bands on each side of the *D*-line. If these two ratios should become equal at two points on each side of the *D*-line, we know that we shall have chromatic compensation for all three colors. Should we fail to find this condition satisfied, we may shift the region of coincidence with the air-bands to some other point and examine for a closer approximation of the ratios, and so on. Very close approximations to such ratios are now possible with certain combinations of the silicate and borate glasses, such as those obtainable from the Jena factory. Compare, for example, factory Nos. 0.152 and S.7, whose partial dispersions for $A' - D$, $D - F$, $F - G'$ are .628, .708, .582 and .628, .708 and .583 respectively. The facility with which comparisons may be made with different experimental castings in obtaining new series and pairs of glasses is evident from the above discussion.

The treatment for media with plane surfaces, *i. e.*, achromatic prisms, is similar to that for curved surfaces or lenses. Thus in the case of two thin prisms, we have to satisfy equations (14) and (15). We obtain, as before,

$$\begin{aligned} \frac{\partial N_0}{\partial s} &= \frac{\mu_0}{\lambda}\frac{\partial l_0}{\partial s} = \frac{\mu_0}{\lambda}\tan i = \frac{\mu_0}{\lambda} i \\ \frac{\partial N_1}{\partial s} &= \frac{\mu_1}{\lambda}\frac{\partial l}{\partial s} = -\frac{\mu_1}{\lambda}\tan a = \frac{\mu_1}{\lambda} a_1 \qquad (49) \\ \frac{\partial N}{\partial s} &= \frac{\mu}{\lambda}\frac{\partial l}{\partial s} = \frac{\mu}{\lambda}\tan i' = \frac{\mu}{\lambda} i'. \end{aligned}$$

where i is the angle of incidence and a that of the prism. From (14) we have

$$\frac{\partial N}{\partial s} = \frac{\partial N_0}{\partial s} + \frac{\partial N_1}{\partial s} + \frac{\partial N}{\partial s} = \frac{\mu_0}{\lambda} i - \frac{\mu_1}{\lambda} a_1 + \frac{\mu}{\lambda} i' = 0.$$

Making $\mu_0 = \mu = 1$, we have, calling D the deviation,

$$i + i' - \mu_1 a_1 = 0 \qquad (50)$$

or, since $D = i + i' - a$, we must have

$$D = (\mu_1 - 1)\, a_1. \qquad (51)$$

Similarly for two prisms we should find

$$i_1 + i_1' - \mu_1 a_1 + i_3 + i_3' - \mu_3 a_3 = 0, \tag{53}$$

or

$$D = (\mu_1 - 1)\, a_1 + (\mu_3 - 1)\, a_3. \tag{54}$$

Differentiating (49), we have

$$\left.\begin{aligned}
\frac{\partial^2 N_0}{\partial\lambda\partial s} &= \frac{i_1}{\lambda}\frac{\partial\mu_0}{\partial\lambda} - \frac{\mu_0 i_1}{\lambda^2}\\
\frac{\partial^2 N_1}{\partial\lambda\partial s} &= -\frac{a_1}{\lambda}\frac{\partial\mu_1}{\partial\lambda} + \frac{\mu_1 a_1}{\lambda^2}\\
\frac{\partial^2 N_2}{\partial\lambda\partial s} &= \frac{i'}{\lambda}\frac{\partial\mu_2}{\partial\lambda} - \frac{\mu_2 i_1'}{\lambda^2}\\
\frac{\partial^2 N_2}{\partial\lambda\partial s} &= \frac{i_3}{\lambda}\frac{\partial\mu_2}{\partial\lambda} - \frac{\mu_2 i_3}{\lambda^2}\\
\frac{\partial^2 N}{\partial\lambda\partial s} &= -\frac{a_3}{\lambda}\frac{\partial\mu_3}{\partial\lambda} + \frac{\mu_3 a_3}{\lambda^2}\\
\frac{\partial^2 N}{\partial\lambda\partial s} &= \frac{i_3'}{\lambda}\frac{\partial\mu_4}{\partial\lambda} - \frac{\mu_4 i_3'}{\lambda^2}.
\end{aligned}\right\} \tag{55}$$

If we make $\mu_0 = \mu_2 = \mu_4 = 1$, we still have

$$\frac{\partial^2 N}{\partial\lambda\partial s} = -\frac{1}{\lambda^2}\left\{\lambda\left[a_1\frac{\partial\mu_1}{\partial\lambda} + a_3\frac{\partial\mu_3}{\partial\lambda}\right] + [i_1 + i_1' + i_3 + i_3' - \mu_1 a_1 - \mu_3 a_3]\right\} = 0 \tag{56}$$

or from (53)

$$a_1\frac{\partial\mu_1}{\partial\lambda} + a_3\frac{\partial\mu_3}{\partial\lambda} = 0. \tag{57}$$

It is evident from this equation that the angles a_1 and a_3 must have opposite signs. We may proceed to a higher order of achromatism by using a greater number of prisms, just as with lenses, obtaining equations similar to (39) and (40). Or we may reduce the residual chromatism in a pair of prisms by satisfying the equation (48) in addition to (53) and (57).

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THE RATE OF RECOMBINATION OF THE IONS IN AIR.

By L. L. Hendren.

If a gas is ionized by any ionizing agent such as Röntgen or radium rays the positive and negative ions will immediately begin to recombine due to their motion and mutual attractions. A simple law, first suggested by J. J. Thomson and Rutherford[1] and obtained by analogy from the law of mass action in physical chemistry, has been found to cover this phenomenon. It states that the rate of disappearance of either charge is proportional to the positive and negative electrical densities, p and n. Thus

$$\frac{dp}{dt}=\frac{dn}{dt}=-anp \qquad (1)$$

where the proportionality factor a is called the coefficient of recombination.

If p and n represent the number of ions per c.c. instead of the charges on these ions the coefficient will be the a above times e, the charge on one ion.

Rutherford,[2] McClung[3] and Langevin[4] have investigated this law with the conclusion that it is a true one, while Townsend,[5] McClung and Langevin have determined the value of the coefficient α for several gases, agreeing with each other as to its value well within the experimental error at atmospheric pressure. For the variation of a with the pressure however, which has been taken up for air by McClung and Langevin, the agreement has not been so good; McClung coming to the conclusion that the coefficient of recombination is independent of the pressure, while Langevin obtained a rapid decrease.

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[1] Phil. Mag., V., 2, p. 92, 896.

[2] Phil. Mag., Nov., 1897, p. 44; Jan., 1899.

[3] Phil. Mag., March, 1902.

[4] Thèse présentée à la Faculté des Sciences.

[5] Phil. Trans. Roy. Soc., p. 157, 1899.

The purpose of the present investigation was to obtain additional data as to the variation of the coefficient of recombination with the pressure, also to obtain values below the limits of pressure previously used.

The results of the work given in a later paragraph show that a decreases with the pressure, though not so rapidly as Langevin's results would indicate. Determinations were made down to 10 mm. pressure as compared with 100 mm. and 150 mm., the limits reached by McClung and Langerin respectively. Values of the coefficient of diffusion of the ions were also obtained at 20 and 10 mm. pressure.

METHOD OF MCCLUNG.

Calling q the total charge on the ions, positive or negative, produced per second by the ionizing agent in each c.c. of the gas, and assuming that there is an equal number of positive and negative ions in each c.c.

$$\frac{dn}{dt} = q - an^2. \tag{2}$$

Thus after the ionization begins the number of ions in the gas will constantly increase until a state of equilibrium is reached between the rate of recombination an^2 and the rate of production q, *i. e.*, until $dn/dt = 0$, when we have the relation

$$a = \frac{q}{n^2}, \tag{3}$$

or if Q and N represent the volume integrals of q and n in a certain volume V

$$a = \frac{Q}{N^2} K, \tag{4}$$

where K is a constant depending upon the dimensions of the vessel used as an ionization chamber, and determined by the distribution of the ionization. If the ionization is uniform $K = V$. Using this formula McClung made a direct determination of a. His ionizing agent was the Röntgen rays which ionized the gas contained in a cylindrical vessel 20 cm. long and separated into ten compartments by thin aluminum partitions. The alternate partitions were connected to each other and acted as electrodes. The Q above, which is the saturation current, was determined in the usual way by noting, by means of the movement of an electrometer needle, the rate of charge of a known capacity connected in parallel with the electrometer and one set of electrodes, against which the ions were being driven by a saturation potential.

The instantaneous value of the free charge N was measured by allowing the Rōntgen rays to ionize the gas until a steady state was reached, then stopping the ionization by breaking the primary circuit of the induction coil, and simultaneously with the stopping of the rays, throwing on a saturation potential across the electrodes, thus driving all the ions present in the gas against the electrodes. The charge N on these ions was obtained by noting on an electrometer the potential to which a known capacity was raised.

METHOD OF LANGEVIN.

Langevin's experimental determination of α is based on a very important theory in which he proves that practically all of the recombination of the ions can be accounted for by the consideration of their mutual attractions. On this basis he obtains the formula

$$\alpha = 4\pi(k_1 + k_2)\varepsilon$$

in which $(k_1 + k_2)$ is the sum of the specific velocities of the ions and ε is the fraction of the whole number of collisions which result in recombination. The $k_1 + k_2$ was measured directly while ε was obtained from experiments based on a further consideration of the theory of ionization. The velocities of the ions increase with decreasing pressure and the ε, due to the large kinetic energy of the ions for long free paths, decreases, thus theoretically it cannot be predicted whether α should decrease with decreasing pressure or not. Langevin as stated before found a rapid decrease.

METHOD AND DESCRIPTION OF THE APPARATUS.

The method adopted in the present case is similar to that of McClung's in that it depends upon the formula

$$a = \frac{Q}{N^2} K,$$

but differs from his in that radium was used as the ionizing agent and the N was determined in a new way. For the determination of N, the charge on the ions present in the gas at any time after a steady state has been reached, it was not attempted to stop the ionization, but the electromotive force was allowed to act across the electrodes for varying intervals of time and the charges thus obtained were corrected for the rate of production during that time.

By the use of radium a great ionization compared with that possible from Röntgen rays can be obtained. Also the very serious difficulty of the inconstancy of the radiation, encountered by other observers in the use of Röntgen rays, is avoided, as the intensity of the radium radiations are very constant after the radium has reached a steady state. The chief objection to its use is the error brought in by the uneven distribution of the ionization due to the absorption of the rays. This will be discussed later.

The diagrammatic arrangement of the apparatus is shown in Fig. 1.

A and B are two aluminum plates, respectively 26 and 30 cm. in diameter, supported and insulated by hard rubber and mounted inside a large glass bell-jar. Both A and B were coated as uniformly and equally as possible with a solution of very active radium chloride, about one milligram of the salt being in the solution. In a majority of the experiments A and B were 6 cm. apart. An aluminum ring G, 1.5 cm. wide, was placed around A with .5 cm. space between. This ring was also coated with radium and acted as a guard ring, tending to make the ionization of the volume of gas under the plate A more uniform with respect to the plane of the plates. G was kept grounded so that only the ions directly under A would be driven into A by a potential on B. Those ions contained in the volume extending out half way between A and G were assumed to be caught by A, thus making the effective area 572 sq. cm. The upper plate A was connected through the key K_2 to the variable known capacity C and this was connected through the key K_1 in parallel with the electrometer, which was of the

Dolazalek type. For the purposes of the experiment it was necessary to be able to apply an electromotive force to the electrode B for varying intervals of time. To accomplish this the plate B was connected in series with a very high resistance to one terminal of a variable high potential source, the other end of which was grounded. A second circuit was run from B to the earth through the break-circuit key T_1 and the make circuit key T_2. Both T_1 and T_2 were placed on adjustable mounts in the path of a pendulum swinging in the path indicated by the arrow. By this arrangement when either T_1 or T_2 was closed B was at zero potential and at the potential of the battery for T_1 and T_2 both open. The pendulum arrangement was calibrated so that the electromotive force could be thrown across B–A for intervals of time varying from .1 to .4 second.

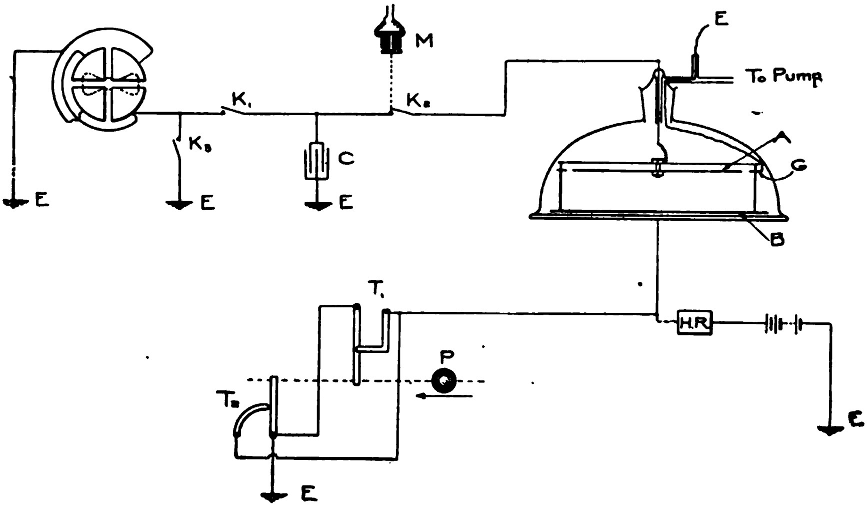

Fig. 1.

Method of Observation.

The saturation current Q was obtained in the usual way by noting on the electrometer the rate of increase of the potential of the known capacity C with the time. A correction was applied to allow for the leak from the plate A to the guard ring. This correction was not large as A was never charged to more than one half a volt.

Care was always taken to have a sufficient potential across B–A to drive out the ions as fast as they were produced, thus getting a true saturation current. Due to the large ionization at high pressures, the saturation potential was very high, 6,000 volts being necessary at atmospheric pressure for the plates 6 cm. apart. The method of experimenting for the determination of N, the amount of free electricity on the ions after the gas has reached a steady state was as follows: First, the capacity C was placed at a suitable value, the three keys, K_3, K_2 and K_1 were closed, as was also the break contact key T_1, thus grounding the system. T_2 was left open and a distance corresponding to .1 sec. left between T_1 and T_2. The pendulum was now swung and at the same time the key T_1 was automatically opened, insulating the capacity and electrode A. When the pendulum opened T_1 the ground was removed and the potential of the battery was across B–A for .1 sec., until T_2 was closed. Thus a certain charge was thrown into the capacity, consisting of the quantity of free charge N_1 on the ions in the gas plus the amount on the ions produced by the radium radiation during .1 sec. Simultaneously with the closing of the key T_2, another circuit, not shown in the figure, was closed, thus actuating the electromagnet M which opened the key K_2 and so insulated the capacity C containing the charge. This was done in order to make the leak back through the ionized gas as small as possible. The time from the closing of T_2 to the opening of K_2 was about .1 sec. The charge on C was now measured by closing the key K_1 and noting the deflection on the electrometer. The operation was now repeated with the potential across B–A for .2 sec., giving a second charge consisting of the N as before plus the charge produced for .2 sec. Thus by taking several successive equal intervals of time, throws were obtained which when carried back to zero time gave the throw corresponding to N. A complete set of such readings for air at 100 mm. pressure is given in Table 1 and the resulting curve by the dotted line in Fig. 2. The throws as indicated on the electrometer need two corrections; one for the loss of charge due to the leak back through the ionized gas during the .1 sec. elapsing between the closing of T_2 and the opening of K_2; the second for the leak from the plate A to the guard ring, which begins to come in when T_1 is opened and continues with increasing value until K_2 is opened. The amount of these corrections depends upon the potential to which C and A are charged and are therefore larger for the longer intervals. The full line in Fig. 2 shows the curve corrected for these two errors. It is seen there that although the corrections may be quite large they effect the value obtained for N comparatively little, merely increasing the slope of the line. For the given pressure, 100 mm. these errors were nearly at a maximum, being much smaller at higher pressures and not so very much larger at the smallest pressures used.

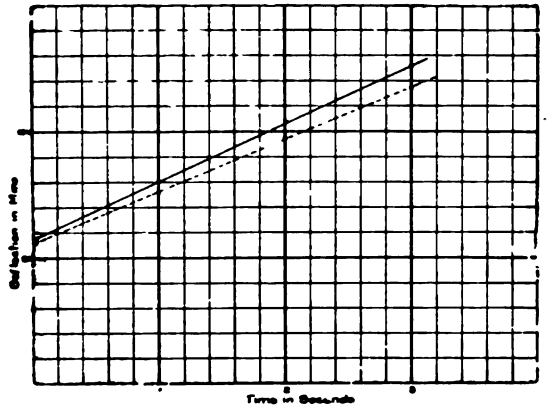

Fig. 2.

By this method of obtaining N, all disturbances, such as leaks across the electrodes, irregularities in the ionization due to secondary actions of the radiation at the plates or other causes, were eliminated, as they tended merely to effect the slope of the line and not the place where it cuts the axis. The regularity of the readings is shown by the example in Table I. These readings could be repeated at any time fairly closely.

Table I.

Illustrative Set of Readings.

Pressure 100 mm. Distance between plates 6 mm. Volume 3435 c.c. Sensitiveness of electrometer 224 divisions for 1 volt on quadrants and 52 volts on needle.

For the saturation current Q: Capacity = .9 microfarads. Volts across plates 440. Time for 30 div., 14 secs. Leak to guard ring 1.6 divs. in 14 secs.

$Q = 31.6$ divs. in 14 secs. $= 27.2$ E. S. units per sec.

For N: Sensitiveness, 224 divs. for 1 volt. Capacity .0102 M.F.

Time E.M.F. Acted Across Plates (Secs.).	.1	.2	.3
Scale divisions.	76 77 76 78 76	97 98 96.5 99 97	117 118 119 116.4 116
Average.	76.6	97.5	117.3
Leak back through ionized gas.	2.5	3.2	3.9
Leak to guard ring.	.8	2.4	4.4
Corrected average.	79.9	103.1	125.6

Rate of leak back through ionized gas 32 divs./sec. at 100 divs. deflection. Time of leak .1 sec. Rate of leak to guard-ring 12 divs./sec. at 100 divs. deflection.

$$\therefore N \text{ (see Fig. 2)} = 57.2 \text{ divs.} = 7.76 \text{ E. S. units.}$$

$$a = \frac{Q}{N^2} V = 1{,}550.$$

Care was taken to have the air dry and dust-free by passing it through phosphorus pentoxide and cotton wool before letting it into the pump and vessel. Also the question of a saturation potential for N had to be carefully looked into, as it was found that it took a higher potential to insure a maximum throw for N than it did for Q at the same pressure.

DISTRIBUTION OF THE IONIZATION.

It is evident that with a certain rate of production the number of ions in the gas between the plates for a steady state will depend upon the distribution of the ionization. For by equation (1), the number of ions disappearing per sec. in one c.c. varies as the square of the number present, therefore a steady state will be reached with a smaller value of N for large ionization gradients than for small ones. To take this into account it is necessary to know the law of the distribution of the ions.

Rutherford[1] has shown experimentally that the intensity of the ionization due to a large plane surface of active matter, such as radium or uranium, falls off approximately according to an expo-

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[1] Phil. Mag., Jan., 1899; "Radioactivity," p. 56.

when T_1 is opened and continues with incr
opened. The amount of these corrections d
tial to which C and A are charged and ar
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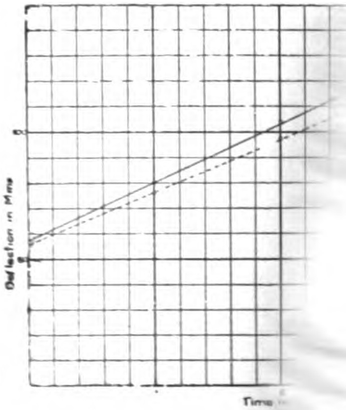

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Q Calculated for λ = .05.
106
86.6
70.8
44

therford[1] to vary approx-
bsorbing matter. There-
p_1 and λ its value at 760
varies as the pressure

$$2a\lambda p_1/760) \qquad (7)$$

he pressure p_1 and q_0' the rate
surface at 760 mm. pressure.
of the saturation current with
d values of this variation, also
iven in Table III.

III.

art. $a = 30$ *mm.*

Q bserved.	Q Calculated for λ = .05.
106	106
101	101.5
94	94
77	78
55	60.7
28.2	36.7
14.2	

Radioactivity," p. 137.

nential law with the distance from the plates, *i. e.*, calling q the rate of production of the ions per c.c. at a point distant y from the active plate

$$q = q_0 e^{-\lambda y},$$

where q_0 is the rate of production at the surface and λ the absorption constant. This result is deduced theoretically on the assumption that the ionization is proportional to the intensity of the radiation and that the energy of the rays is used up in producing ions. Bragg[1] later on showed that this exponential law is not necessarily a true one, but might hold very closely for the complex radiations from radium spread over a large surface.

In the present case we have rather complex conditions, the ionization being due chiefly to the α rays from the radium on the two plates, but the β rays and the radiation from the emanation throughout the volume of the gas also play some part. To obtain the actual distribution the exponential law was assumed and experiments made to find out how closely it held and for what value of λ.

Taking the origin of coördinates half way between the plates which are $2a$ cm. apart, and the axis x at right angles to the plane of the plates, we have by the exponential law

$$q = q_0 e^{-\lambda(a-x)} + q_0 e^{-\lambda(a+x)} \tag{5}$$

each factor being the contribution of one plate to the ionization q at the point x.

Taking the volume integral of q

$$Q = \int q dv = A \int_{-a}^{+a} q_0 [e^{-\lambda(a-x)} + e^{-\lambda(a+x)}] dx,$$

A being the area of one plate.

Integrating,

$$Q = 2Aq_0 \frac{1 - e^{-2\lambda a}}{\lambda}. \tag{6}$$

Using this equation and obtaining saturation currents for different distances between the plates it was found that the conditions were closely satisfied for the value $\lambda = .05$, a being expressed in millimeters. This value of λ was obtained by taking any two distances with the corresponding Q's, giving two equations of the form of (6) from which q_0 was eliminated. Knowing λ and starting with the Q for 60 mm. distance the other Q's can be calculated. These values are shown in Table II.

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[1] Phil. Mag., Dec., 1904.

TABLE II.

Pressure 760 mm.

Distance Between Plates.	Q Observed.	Q Calculated for $\lambda = .05$.
60 mm.	106	106
30	87	86.6
20	70.8	70.8
10	45.6	44

The constant λ has been found by Rutherford[1] to vary approximately inversely as the density of the absorbing matter. Therefore calling λ_1 the constant at a pressure p_1 and λ its value at 760 mm., we can write eq. (6), since q_0 also varies as the pressure

$$Q_1 = 2Aq_0'\left(1 - \epsilon^{-2a\lambda p_1/760}\right) \qquad (7)$$

Here Q_1 is the saturation current at the pressure p_1 and q_0' the rate of production per c.c. at the radiating surface at 760 mm. pressure. This equation expresses the variation of the saturation current with the pressure of the gas. Observed values of this variation, also values calculated for $\lambda = .05$, are given in Table III.

TABLE III.

Plates 60 mm. apart. $a = 30$ mm.

Pressure.	Q Observed.	Q Calculated for $\lambda = .05$.
760	106	106
600	101	101.5
450	94	94
300	77	78
200	55	60.7
100	28.2	36.7
50	14.2	

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[1] "Radioactivity," p. 137.

Fig. 3 shows these values plotted. The full line curve shows the observed variation of Q with the pressure, the dotted line the calculated variation. At high pressure the coincidence is very close. Thus we are justified in assuming that at high pressures at least the distribution is given by the exponential law with .05 as the value of the absorption constant. Below 300 mm. pressure the curve is nearly a straight line and the ionization is practically uniform, and so we need no correction.

The value of $\lambda = .05$ obtained here is much smaller than the value .9 given by Rutherford[1] as the absorption constant for the α-rays from radium. His value, however, was obtained by a somewhat different method, under different experimental conditions from the ones used here. In his work radiferous barium was used and the ionization measured after a good part of the radiation had been absorbed by passing through air and aluminium, thus getting a portion of the more easily absorbed α-rays. Also the curves given by Rutherford[2] for variation of the saturation current with the pressure between two large parallel plates, one of which was active, fall

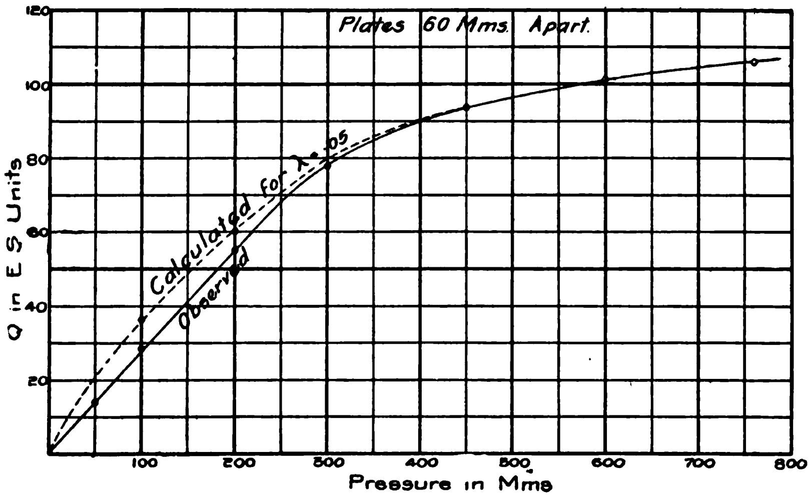

Fig. 3.

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[1] "Radioactivity," p. 137.

[2] Phil. Mag., Jan., 1899, pp. 130, 138.

off much more rapidly than his theory would indicate, using such a large value of λ.

CORRECTION TO a FOR UNEVEN DISTRIBUTION OF THE IONIZATION.[1]

Suppose n as before to be the electric density of the free charge at the point x when a steady state has been reached. Taking the volume integral

$$N = \int n dv,$$

but by equations (3) and (5)

$$n = \sqrt{\frac{q}{a}} = \sqrt{\frac{q_0}{a}(e^{-\lambda(a-x)} + e^{-\lambda(a+x)})},$$

therefore

$$N = A\left(\frac{q_0}{a}\right)^{\frac{1}{2}} \int_{-a}^{a} [e^{-\lambda(a-x)} + e^{-\lambda(a+x)}]^{\frac{1}{2}} dx.$$

But as the ionization is symmetrical out from the middle point toward either plate the lower limit can be changed from $-a$ to 0 if the integral is multiplied by the factor 2. Doing this, and rewriting

$$N = 2A\left(\frac{q_0}{a}\right)^{\frac{1}{2}} e^{-\frac{1}{2}\lambda a} \int_0^a e^{\frac{1}{2}\lambda x}(1 + e^{-2\lambda x})^{\frac{1}{2}} dx.$$

Expanding $(1 + e^{-2\lambda x})^{\frac{1}{2}}$ by the Binomial Theorem, multiplying by $e^{\frac{1}{2}\lambda x}$, integrating the series term by term and simplifying we have

$$N = 2A\left(\frac{q_0}{a}\right)^{\frac{1}{2}} \frac{1}{\lambda}\left[\left(4 - \tfrac{2}{3}e^{-2\lambda a} + \tfrac{1}{14}e^{-4\lambda a} + +\right) - e^{-\frac{1}{2}\lambda a}\left(4 - \tfrac{2}{3} + \tfrac{1}{14} + +\right)\right].$$

Since in these experiments λ is .05 and a 30, λa has the value .15, and both of these series are rapidly converging, therefore a close approximation is obtained by neglecting all except the first two terms of the first series and taking 3.38 as the sum of the second. Thus

$$N = 2A\left(\frac{q_0}{a}\right)^{\frac{1}{2}} \frac{4 - \frac{2}{3}e^{-2\lambda a} - 3.38e^{-\frac{1}{2}\lambda a}}{\lambda}.$$

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[1] See McClung's article, loc. cit.

But from equation (6)

$$q_0 = \frac{\lambda Q}{2A(1 - e^{-2\lambda a})}.$$

Substituting this value and solving for a

$$a = \frac{Q}{N^2} A \frac{(4 - \frac{2}{8}e^{-2\lambda a} - 3.38e^{-\frac{1}{2}\lambda a})^2}{2\lambda(1 - e^{-2\lambda a})}.$$

The exponential term in this equation should be equal to 6, the number of cm. between the plates for uniform ionization. For the value $\lambda a = .15$ this term becomes equal to 5.9. Therefore even at atmospheric pressures the correction for uneven distribution is very small and a can be taken equal to QV/N^2 where V is the volume of gas between the plates.

Effect of Diffusion at Low Pressures.

At above 100 mm. pressure it was found that with the plates 6 cm. apart the loss of ions due to diffusion to the plates and sides of the vessel was negligibly small compared with the loss due to recombination proper. Below this pressure however the observed N began to decrease very rapidly due to diffusion and

$$\frac{Q}{N^2} V$$

to increase correspondingly. It is easily seen how this would come about, since if the loss of ions due to diffusion is appreciable a steady state will be reached for a smaller value of N than it would if there was no such loss.

Due to diffusion there will be an ionization gradient along x from the plane midway between the plates out to their surfaces, where there will be no ionization, the ions there present giving up their charges to the plates. The charge on the ions crossing unit area in unit time due to the gradient dn/dx will be $D\,dn/dx$, where D is the coefficient of diffusion. Therefore the rate of increase of free charge in any unit volume will be $D\,d^2n/dx^2$. Thus for a steady state

$$q = an^2 - D\frac{d^2n}{dx^2}.$$

A satisfactory solution of this equation is not easily found, but for the special case where the factor due to recombination is negligibly small, J. J. Thomson[1] gives the solution

$$n = \tfrac{1}{2}\frac{q}{D}(a^2 - x^2),$$

from which

$$N_0 = \tfrac{1}{3}\frac{qa^2}{D}, \qquad (8)$$

$2a$ being the distance between the plates.

This N_0 represents the charge on the ions which would be in the gas for a steady state if the ions disappeared by diffusion only. The coefficient of diffusion D has been shown by Townsend[2] to vary inversely as the pressure down to 200 mm. so that the loss due to diffusion increases as the pressure decreases. Also it is seen that the diffusion effect varies inversely as the square of the distance between the plates.

This rapid increase of the diffusion effect as the plates get close together was used to get an idea of the error in the observed N brought in by diffusion.

A series of determinations of N and Q were made for different distances between the plates. These results are shown for pressures of 50, 20 and 10 mm. in tables IV.–VI. The fourth column of these tables show the very rapid rise, with the small distances, of the quantity $Q/N^2\,V$ which would be α, the coefficient of recom-

Table IV.

Area of Plate, 572 *sq. cm.* *Pressure*, 50 *mm.*

Distance Between Plates.	Q.	N.	$\frac{Q}{N^2}V = \alpha'$.	N_D.
8 cm.	16	7.4	1,340	160
6	14.2	5.9	1,380	80
3	7.64	2.9	1,570	16
2	5.7	1.9	1,830	4

Limiting value of α' is $\alpha = 1{,}310$.

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[1] J. J. Thomson, "Conduction of Electricity through Gases," p. 20.

[2] Townsend, Phil. Trans., A, 195, p. 2 9, 1900.

TABLE V.

Pressure, 20 *mm.*

Distance Between Plates.	Q.	N	$\frac{Q}{N^2} V = \alpha'$.	N_D.
8 cm.	6.4	4.75	1,290	25.6
6	4.7	3.14	1,600	10.5
3	3.0	1.14	4,000	1.7
2	2.3	.52	10,000	.58

Limiting value of $\alpha' = \alpha = 1{,}150$.

TABLE VI.

Pressure, 10 *mm.*

Distance Between Plates.	Q.	N.	$\frac{Q}{N^2} V = \alpha'$.	N_D.
8 cm.	3.1	2.7	2,100	6.2
6	2.4	1.4	4,000	2.7
3	1.6	.38	19,000	.45
2	1.21	.143	68,000	.15

Limiting value of $\alpha' = \alpha = 1{,}000$.

bination, if all the loss of ions was considered due to recombination. It is evident that if there was no diffusion, this quantity $Q/N^2 V$, which will be called the apparent α and denoted by α' would be independent of the distance between the plates.

To obtain α at each pressure a curve was plotted between α' as ordinate and the distances between the plates as abscissa, and the value of α' for which this curve became a straight line parallel to the horizontal axis was taken as the true coefficient of recombination. These curves are shown in Fig. 4.

At 50 mm. pressure it is seen that diffusion makes very little error in α even when the plates are 2 cm. distance apart, while at 10 mm. pressure for the small distances between plates it has a very great effect, the loss of ions due to diffusion evidently exceeding that due to recombination. The values of α finally adopted and given in Tables IV.–VI. were taken from these curves plotted on a much larger scale.

A good idea of the way in which diffusion and recombination enter at the different pressures and distances may be obtained by a consideration of the experimental values of N in the Tables IV.–VI. and the values given in the last column headed N_D. This N_D is the value of N which would have been expected if the loss of the ions balancing the rate of production Q was due to diffusion only. They are calculated from equation (8) taking the coefficient of diffusion D at Townsend's value of .035 for atmospheric pressure and assuming it to vary inversely with the pressure. The larger the value of N_D compared with N the less the effect of diffusion. Thus at 50 mm. pressure and the plates 8 cm. apart, diffusion plays very little part, but at 10 mm. pressure for the plates 2 cm. apart it accounts for nearly the entire loss of ions.

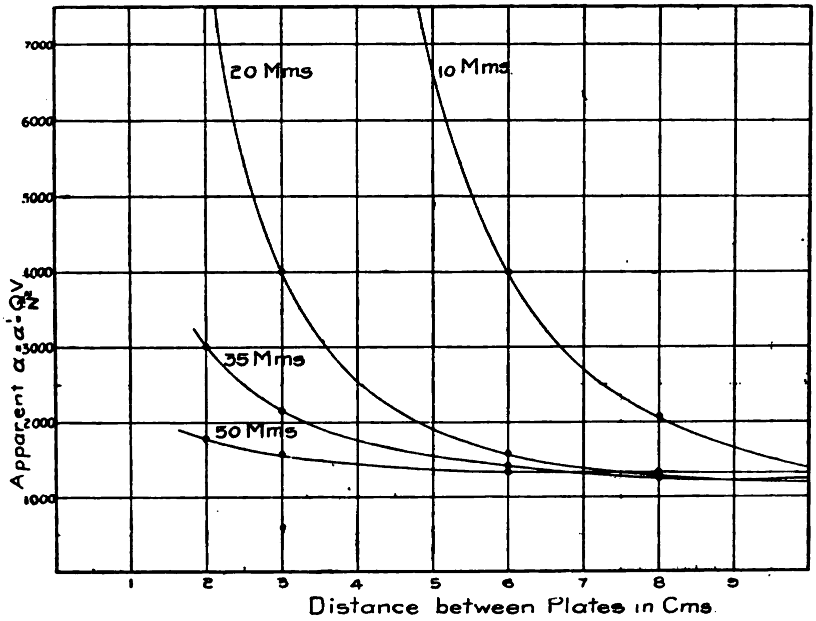

Fig. 4.

For pressures below 10 mm. pressure and with vessels of ordinary dimensions as in discharge tubes, for instance, practically all of the ions disappear by diffusion to the sides of the vessel.

THE COEFFICIENT OF DIFFUSION AT LOW PRESSURES.

For 20 mm. and 10 mm. pressures and for the small distances between the plates diffusion has been seen to play the important part. Proceeding in a manner analogous to the method adopted for getting a separate from the diffusion error,it is possible to get a fairly good value for the coefficient of diffusion D at these pressures. Thus it is evident that the coefficient of diffusion, which is given by the equation

$$D = \frac{1}{8}\frac{Q}{N}a^2,$$

when there is no recombination, is a constant at any pressure and should not depend upon the distance between the plates. If, using the experimental values for Q and N, D apparently increases with the distances between the plates, it means that, due to recombination, the experimental N is smaller than it would be for diffusion loss only. The relative loss due to recombination should increase with the distances between the plates. Fig. 5, plotted from the values in the tables VII. and VIII. shows the increase of this apparent D with the distances between the plates.

TABLE VII.

Pressure, 20 *mm.*

Distance Between Plates.	Q.	N.	$\frac{1}{8}\frac{Q}{N}a^2 = D'$.
8 cm.	6.4	4.75	7.1
6	4.7	3.14	4.4
3	3.0	1.14	1.9
2	2.3	.52	1.4

TABLE VIII.

Pressure, 10 *mm.*

Distance Between Plates.	Q.	N.	$\frac{1}{8}\frac{Q}{N}a^2 = D'$.
8 cm.	3.4	2.7	6.8
6	2.38	1.4	5.0
3	1.6	.38	3.2
2	1.21	.143	2.8

As in the curves for a, where the D' becomes constant with the distance between the plates is taken as the coefficient of absorption at that pressure. In this manner D was found to have the value 11. at 20 mm. pressure and 2.6 at 10 mm.

Reducing these values back to atmospheric pressure on the assumption that *D* varies inversely with the pressure, we get the values .030 and .034. Townsend found (*loc. cit.*) that *D* varied inversely with the pressure down to 200 mm. pressure and his value at atmospheric pressure was .035. The two values given above thus indicate that *D* continues to vary inversely with the pressure at least down to 10 mm.

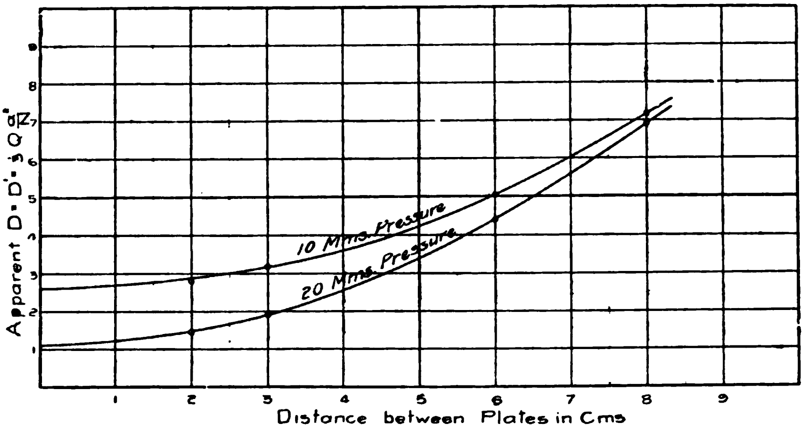

Fig. 5.

As, by theory, *D* varies directly with the specific velocities of the ions this would indicate that the velocities too are a linear function of the pressure down to 10 mm. J. Stark[1] gives some results showing this, but Langevin[2] has found that the velocities increase with decrease of pressure faster than a linear law would allow.

Variation of *a* with the Pressure.

The complete results for the variation of *a* with the pressure are given in Table IX. and plotted in the form of a curve in Fig. 6. The values of *a* here given are the mean of several determinations. The values of *N* given in the table are not in every case the ones from which the corresponding *a* was obtained, as some of the determinations were made before the radium had reached a steady state.

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[1] J. Stark, Die Electricität in Gasen, p. 261.

[2] M. Langevin, Thèse, p. 140.

TABLE IX.

$V = 3{,}435$ c.c.

Pressure.	Q.	N.	$a = \frac{Q}{N^2} V$.
760 mm.	106	10.5	3,300
450	94	11	2,650
250	67	10.6	2,070
150	42.2	9.1	1,750
100	28	7.9	1,550
50	14.2	6.1	1,310
35	10	5.2	1,250
20	5.6	4.1	1,150
10	3.0	3.2	1,000

At atmospheric pressure the value of a has been previously well fixed. Townsend obtained 3,400, McClung 3,384 and Langevin 3,200 as the absolute value of a. The value 3,300 given here is seen to agree very closely with these results.

As to the variation of a with the pressure the curve in Fig. 6 shows that a decreases to a value 1,000 at 10 mm. pressure, the rate of decrease constantly increasing as the pressure falls.

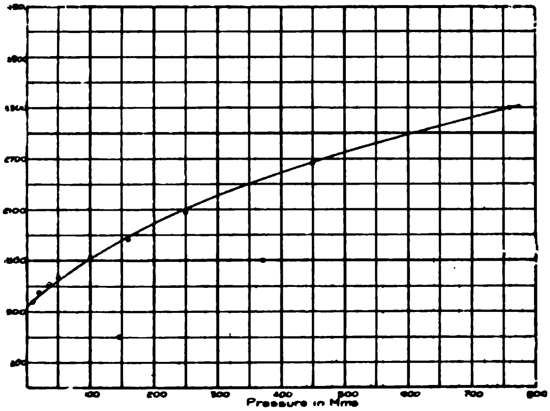

Fig. 6.

Coefficient of Recombination a.

The curve falls below that of McClung's who found a independent of the pressure down to about 100 mm. It goes above that of Langevin who found a somewhat more rapid decrease. Langevin does not give the absolute value of α obtained at pressures below atmospheric, but does give the data for 375 and 152 mm. for which the values 1,500 and 600 have been calculated. These values are indicated in Fig. 6 by two × marks.

It is difficult to compare the present results as to accuracy with those of Langevin as his experimental work was based on a rather complicated theory. In a general way Langevin's results are confirmed as there is a decrease of α with the pressure.

With McClung's results however a comparison can be made as both methods were direct ones. Langevin makes the following legitimate criticisms of the experimental conditions under which McClung worked.

The intensity of the Röntgen rays vary considerably in very short intervals of time, thus making it necessary to take the average of very many widely divergent readings. Also the ionization is very small even at high pressures, rendering accurate determinations of the charges difficult.

An error is introduced by not knowing the exact distribution of the ionization. Also the effect produced by the secondary radiations emitted by the metal plates under the action of the Röntgen rays is considerable and continues after the Crookes tube has been stopped.

Loss of ions by diffusion to the electrodes also brings in a probable error.

This last source of error might explain to some extent McClung's large values of α for low pressures, as he had a very large surface exposed and the electrodes were close together. This diffusion effect has been shown to come in very rapidly as the distance between the plates and the pressure decrease.

Practically all of these objections except that due to uneven distribution have been met in the present work. The intensity of the radium radiations was very constant and the ionization large and thus the readings could be repeated within a few per cent. The secondary radiations could introduce no error on account of the method of determining N. The diffusion effect was corrected for in those cases where it was appreciable. As for the distribution error, it has been shown that with a somewhat large divergence from a uniform distribution the correction for α is very small, therefore any error in the determination of the distribution could not effect the value of α very much.

In conclusion I wish to acknowledge my indebtedness to Dr. Bergen Davis at whose suggestion this investigation was taken up and with whose advise it was carried on.

Phœnix Physical Laboratory,
Columbia University, May, 1905.

NOTE ON THE IRREVERSIBILITY OF THE HEUSLER ALLOYS.

By Bruce V. Hill.

BEING attracted by the accounts of Heusler's magnetic alloys of copper, manganese and aluminium, the author cast several of these alloys which showed some properties so interesting that it seemed worth while to give a brief preliminary description of them.

It may not be out of place to say something of the history of the discovery of these alloys and of the theory which applies to such cases. It is common to think of iron, cobalt, nickel and bismuth as the only substances having a measurable magnetic susceptibility. As a matter of fact, however, a large number of the elements show either para- or dia-magnetic properties. Stephen Meyer[1] found that some of the rare metals are strongly para-magnetic. The metals themselves were very difficult to obtain in a pure state and in quantities sufficient for the purposes of testing. When the salts of some of them were examined they exhibited even a greater susceptibility than those of iron. Defining the *atomic susceptibility* as the mean susceptibility of a space containing one gram atom of the substance in 1,000 cubic centimeters, Meyer gives the atomic susceptibilities of a number of the elements in the following order: Ho, Er, Gd, Mn, Fe, Sa, Co, Yt, Nd, Ni, Pr.[2] He says that if then, the susceptibility of metallic erbium were as much greater than that of iron as the susceptibility of the oxide is greater than that of the oxide of iron, dynamo-machinery and other apparatus could be built having only one sixth the weight of those of iron for the same output, since the density of erbium is only two thirds that of iron. This premise is not necessarily true, however, for manganese also stands before iron in the above list and it is not magnetic in the ordinary metallic form, though electrolytic manganese was found to be slightly magnetic. It may be possible to account for the different magnetic properties of these metals in their salts and in the metallic condition in a simple manner however.

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[1] Stephen Meyer, Ann. d. Phys , 68, p. 325, 1899.

[2] Stephen Meyer, Ann. d. Phys., 69, p. 236, 1899.

So far as iron and nickel, at least, are concerned there seems to be abundant reason to believe that they can exist in several allotropic forms. This is the "allotropic theory" of Osmond. The facts supporting it can not be enumerated here; a number are given with references in my paper mentioned under 8. In iron there are supposed to be three such modifications: the alpha form, soft, magnetic and stable below 700° to 750° C.; the beta form, hard, unmagnetic and stable between 750° and 860° C.; and the gamma form, soft, unmagnetic and stable above 860°C. In passing one of these transformation points heat is evolved as is seen in the recalescence of steel. In nickel there have been found but two allotropic forms: the alpha form, magnetic and stable below 340° to 360° C., and the beta form, unmagnetic and stable above that temperature.

This temperature of transformation may be depressed by alloying a second metal with the iron or nickel. This depression is proportional to the amount of the alloy as is seen in the case of the alloys of aluminium and iron[1] or of copper and nickel.[2] In this the alloys behave as other solid solutions.[3] This depression of the transformation point is analogous to the depression of the freezing point of a solvent by the dissolved substance.

The allotropic theory explains the phenomena of the tempering of steel as the older theory that the hardening was due to strains set up in the metal by the sudden cooling never did. The compound steels furnish much of interest in this connection, especially the self-hardening and irreversible nickel-steels.[4] The irreversible steels[5] (so-called from the fact that if, starting in the magnetic condition, they be heated to dull redness they become unmagnetic, but on cooling do not regain their magnetic properties until a temperature is reached much lower than that at which they originally became unmagnetic; if the temperature be again raised the material remains magnetic till the original point of transformation is attained) make it possible to compare the properties of these alloys in the magnetic and the unmagnetic conditions at the same temperature. This has been done by a number of experimenters.[1] It appears also that while one allotropic form, the magnetic, is that ordinarily existing at room temperature, it is possible to render the other, the unmagnetic, stable at that temperature.

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[1] Lownds and Richardson, Phil. Mag. (6), 1, p. 601, 1901.

[2] B. V. Hill, Verh. d. Deut. Phys. Gesell. Jahrgang, IV., Nr. 9, 1902.

[3] Bruni, Feste Loesungen, German edition, Stuttgart, 1901.

[4] For a full account of these steels see L. Dumas, Recherches sur les aciers au nickel a haute teneures, Paris, 1902.

[5] Ewing, Magnetization in Iron and Other Metals, p. 185, 1900.

It has been seen that the salts of manganese and chromium are in the same class, so far as the magnetic properties are concerned, with those of iron, cobalt and nickel. Might it not then be conjectured that manganese and chromium also have several allotropic forms or phases, of which it is the unmagnetic with which we are acquainted, but that, if the right alloy could be found, the magnetic form might be had.

Heusler's[9] discovery of such an alloy in the case of manganese seems to have been accidental, however. When working with an alloy prepared for another purpose and with a tool of whose magnetization he was not aware, he found that the alloy was attracted by the tool. He then sought in a systematic way to produce magnetic alloys of manganese. He found that certain of the trivalent elements have a particularly strong effect upon manganese even at comparatively low temperatures. If one part of powdered antimony and four parts of powdered manganese be heated together to 500° or 600° C., which is still far below the melting point of manganese, the mixture becomes noticeably magnetic. I tried a similar experiment with chromium, but without success.

Starting with the commercial alloy of 70 per cent. copper and 30 per cent. manganese, Heusler made several series of alloys using as a third metal tin, antimony, arsenic, aluminium, etc., of all of these the last gave the best results. In the alloys of copper, manganese and aluminium the susceptibility increased until the masses of the manganese and aluminium were in the ratios of their atomic weights, and then grew less again as the amount of aluminium was increased. The magnetic properties of these alloys were investigated by W. Starck and E. Haupt,[1] the magnetic expansion by L. Austin[2] and the effects of prolonged heating and cooling by E. Gumlich.[3] Continued heating at a temperature of 110° C. increased the susceptibility, while annealing at 500° C. left the material practically unmagnetic. Cooling in liquid air had no effect. None of these authors mention a temperature over 580° C.

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[1] Ch. Ed. Guillaume, Comt. Rend., 124, p. 176; 1515, 1897; 125, p. 235, 1897. E. Dumont, C. R., 126, p. 741, 1898 L. Dumas, C. R., 130, p. 1311, 1900. F. Osmond, C. R., 118, p. 532, 1894; 128, p. 304, 1899. H. Tomlinson, Proc. Roy. Soc., 56, p. 103, 1894. J. Hopkinson, Proc. Roy. Soc., 47, p. 23; 138, 189 ; 48, p. 1; 442, 1890, 50, p. 121, 1891. B. V. Hill, Verh. d. Deut. Phys. Gesell., III., Nr. 10, 1901.

[2] Schriften d. Gesell. z. Befoerderung d. gessammt. Naturwiss. zu Marburg, Bd. 13. 5te. Abtheilung, Marburg, 1904. (Verh. d. Deut. Phys. Gesell., 5, 12, p. 220, 1903.)

Of the alloys made by the author one contained about 60 per cent. copper, 25 per cent. manganese and 15 per cent. aluminium, the other a higher per cent. of aluminium. They were made by melting the aluminium with the 30 per cent. manganese-copper alloy, and were cast in the form of rods 0.45 cm. in diameter and 12 cm. long. The metal was very hard and brittle. The magnetic testing was done by the ballistic method. About a porcelain tube 70 cm. long and 2.5 cm. in diameter was wound a nickel heating coil. This was put into a glass tube 5 cm. in diameter and packed about with kaolin. The glass tube fitted closely into a brass water jacket having a space 0.5 cm. between the walls. The magnetizing coil was wound upon this jacket and could thus be kept at a constant temperature even when the interior of the apparatus was very hot. The secondary coil was would upon a smaller porcelain tube which was placed within the heating tube. The specimen, together with one junction of a thermo-element, was within this second porcelain tube and packed with asbestos to prevent heat losses. Corrections were of course made for the demagnetizing effect of the ends of the rod and for the area between the rod and the secondary coil. It may be remarked here that an apparatus of this kind is intended to measure changes of induction with temperature and does not profess to give absolutely accurate values of the induction itself though the error in this respect is not large. M. L. Dumas[4] determined the transformation points of his nickel-iron alloys by merely observing the temperature at which a compass needle near the specimen ceased to be affected by it.

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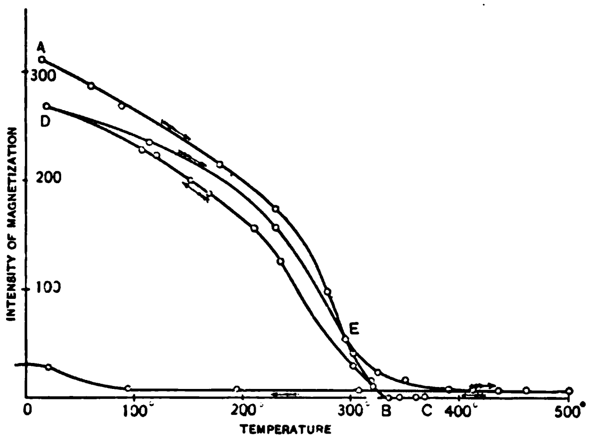
[1] Verh. d. Deut. Phys. Gesell., 5, 12, p. 224, 1903.

[2] Verh. d. Deut. Phys. Gesell., 6, 14, p. 211, 1904.

[3] Ann. d. Phys., 16, p. 535, 1905.

[4] See 6.

The first rod tested was that of higher percentage of aluminium. It showed an induction of $B = 5750$ c.g.s. in a field on $H = 87$ c.g.s. with a comparatively large area of the hysteresis curve. On being heated it behaved as those of the other observers had done (up to 500° C.), yet it may be of interest to give the curves showing the relation of the intensity of magnetization, I, to the temperature as the metal is heated and cooled, since no such have been published. The field was kept constant and equal to 85 c.g.s. A relatively strong field was used to avoid the occurrence of maxiam as in the curves for iron and nickel in weak fields.[1] The general form of the curves here is similar to that for the other magnetic metals and their alloys. Beginning at A with an intensity of $I = 311$ c.g.s. the curve falls till it reaches the axis at B. The temperature was carried 33° higher bringing the curve to C. On cooling the line leaves the axis again at B but does not return to A but to a lower value at D, $I = 267$. With the second heating the curve lies above that for the first cooling and does not come to the axis at B but crosses the former heating curve at E and when



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[1] Ewing, Mag. in Iron, Figs. 79, 85, 8 , 1900.

heated to 500° C. retains a slight susceptibility, I being equal to 7. After falling the second time to 17° C. the intensity was only 27, that is the susceptibility was only 0.32. A reading was taken with the specimen in liquid air, giving $I = 36$. This remained unchanged when room temperature was again reached.

It now occurred to me that, from the general behavior of the alloy, it might be expected that the magnetic qualities of the metal would be restored if it were taken to a temperature considerably higher than those previously attained. The specimen was, therefore, heated, in the flame, to dull redness (650° to 700° C.) and allowed to cool slowly. When tested in the same way as before the intensity was $I = 90$ in the field of $H = 85$. Reheating to the same temperature and cooling rapidly did not alter this value of I. The rod was then heated to a bright red (850° C.?) and when tested at room temperature the intensity was $I = 155$. After cooling in liquid air $I = 162$.

We have here then a new type of irreversible alloy, but in a sense opposite to the irreversible nickel-steels. Compare this with one of the specimens used in the study of the specific heats of some of these nickel-steels.[1] The alloy contained twenty-four per cent. of nickel. Let B_H represent the induction B for the field H at the temperature of the room. The temperatures given are those to which the metal was cooled, or heated, immediately before the induction was determined. For the sake of the comparison $B = H + 4\pi I$ is used instead of the values of I given in the preceding paragraphs. Tabulating the results for the two alloys :

Nickel-steel,				
When received,	0°	$-20°$	$-79°$	$-190°$
Unmagnetic,	$1,200_{136}$	$3,700_{135}$	$9,200_{135}$	$10,200_{136}$
Heusler alloy,				
When cast,	368°	500°	650° ?	850° ?
$4,020_{85}$	$3,440_{85}$	427_{85}	$1,220_{85}$	$2,030_{85}$

In the first case the alloy, after cooling from the temperature of forging, was unmagnetic, but its permeability was found to be greater the lower the temperature to which it had been cooled. Heating to dull redness left it again unmagnetic. In the other alloy the metal was magnetic when first cast. Cooling to very low temperatures had only a very inconsiderable effect. If heated and allowed to cool to room temperature, the permeability varied with the temperature to which it had been carried, showing a minimum in the neighborhood of 500° C. One might venture a further comparison, as the merest conjecture. In the nickel-steel here spoken of, the magnetic state, when cooled from the temperature of the furnace, is that of iron at high temperatures. Dr. D. K. Morris[1] found also that iron regains its susceptibility to a slight degree between 800° and 1000° C. It is then possible that manganese would be found to be magnetic at a sufficiently high temperature.

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[1] Verh. d. Deut. Phys. Gesell., III., Nr. 10, 1901.

Returning to the description of the alloys in hand, the second rod tested was that of lower per cent. of aluminium. It had an induction of $B = 11,800$ in a field of $H = 75$, with very little hysteresis. Its behavior was in general like that of the first one, but, when heated to 950° C. and cooled to room temperature, it remained unmagnetic. There was a great difference in the density of this alloy in the magnetic and in the unmagnetic conditions. When first cast the density was 6.61. After annealing at 950° C. it was but 5.80. Here again the nickel-steels show an opposite change. One of the alloys of nickel and iron referred to above had a density of 7.91 in the magnetic state, 8.09 in the unmagnetic, a change of about 2 per cent. This agrees with the results of H. Tomlinson[2] and J. Hopkinson.[3]

Stephan Meyer found that, when a diminution of volume occurs in a compound, the para-magnetic character of the substance is increased and *vice versa.* In the case of alloys we are, in general, dealing with solid solutions and not with compounds of the constituents, so that the applicability of this statement to alloys would have to be tested by experiment. There is possibly more reason to suspect chemical combination between the manganese and the aluminium in the Heusler alloy than between the iron and the nickel in the nickel-steel, since the permeability of the former is greatest when the percentages of the two metals are proportional to their atomic weights. These alloys are also those which are most dense in the magnetic condition.

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[1] Phil. Mag., 44, p. 213, 1897.

[2] See footnote No. 8.

[3] See footnote No. 8.

ON THE WAVE-LENGTH OF THE RADIATION GIVEN OFF IN AN ALTERNATING CONDENSER FIELD.

By Fernando Sanford.

IN a previous paper by the present writer[1] some measurements were given of the wave-length of the radiation from aluminum, silver, copper and zinc when these metals are joined to the cathode of the secondary of an induction coil or are placed in the field of an air condenser the plates of which are joined to the terminals of an induction coil. Since that time, similar measurements have been made for other metals and for some non-metallic substances. These measurements have been made by means of the grating used in the former experiments, viz., a celluloid replica of a Rowland plane grating having 14,438 lines to the inch.

In all cases here mentioned the radiating substance, the grating and the photographic plate were enclosed in a dark box which was placed between the glass plates upon which the tinfoil condenser sheets were pasted. The radiation was allowed to pass through a slit in a vulcanite screen and through the grating and fall upon the photographic plate. On account of the feeble intensity of the radiation, the slit and grating were placed only from four to five centimeters from the plate, and the distance of the first spectrum from the central image of the slit was only from eight to ten millimeters. Naturally this distance could not be measured with a high percentage of accuracy, but the plates were all re-measured by Miss Shirley Hyatt, a student in the laboratory, and the two measurements seldom differed by more than two or three per cent.

In general, the radiation from each metal seemed very homogeneous. Only in the case of platinum was the spectrum appreciably wider than the central image of the slit. The metals tested and the wave-lengths determined for their radiations are given below.

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[1] Physical Review, XVIII., 366, May, 1904.

Metal.	$\lambda \mu\mu$.	Metal.	$\lambda \mu\mu$
Cadmium,	335	Nickel,	360 (?)
Tin,	340	Iron,	369
Bismuth,	346	Copper,	372
Antimony,	351	Zinc,	380
Magnesium,	348 (?)	Manganese,	380
Aluminum,	350	Lead,	380
Silver,	350	Platinum,	380–400
Gold,	350	Tinfoil,	329

The measurements made on magnesium and nickel were less satisfactory than the others, the photographs of the spectra being less clear. In platinum the width of the diffracted image indicated that the radiation was less homogeneous than in the case of the other metals. Apparently some of this radiation extended to the extreme violet of the visible spectrum. Carbon disulphide was, however, apparently quite opaque to the platinum radiation, indicating that the greater part of the radiation was of wave-length not much greater than 380.

A number of crystals of various salts were tried as radiators by sticking a crystal with glue on a piece of cardboard which was placed upright in the dark box in front of the slit. It was found that in this position the cardboard gave off no appreciable radiation. Of the crystals tried, all gave off the radiation except sodium chloride and nickel sulphate. These gave no appreciable radiation after exposures of from 17 to 25 minutes while from 5 to 10 minutes was generally long enough to give a plain image of the slit. It is interesting to notice in this connection that sodium chloride is one of the salts found by Schmidt[1] not to be actinoelectric. Nickel sulphate is not given in his list.

The following substances gave off radiation of wave-length approximately as given below:

Substance.	$\lambda \mu\mu$.	Substance.	$\lambda \mu\mu$.
Silver nitrate,	334	Potassic bromide,	370
Ferrous sulphate,	weak (?)	Potassic ferrocyanide,	334
Copper sulphate,	363	Cinnabar,	359
Lead nitrate,	348	Sulphur,	(?)

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[1] G. C. Schmidt, Wied. Ann., 64, 708–724.

In the case of radiation from crystals even more than from metals it was found that sharp points or edges were the principal sources of the radiation. Photographs of crystals made by means of their own radiations and by the use of a quartz lens showed only a number of point or line sources of the radiation.

Stanford University,
June, 1905.

TOTAL REFLECTION.

BY ELMER E. HALL.

IN a former article[1] the writer has discussed the theory of penetration during total reflection, when reflection takes place from a thin film contained between two denser media. The discussion was based upon the electromagnetic theory of light and particular application was made to the case of a film between the hypotenuse surfaces of two right-angled glass prisms placed almost in contact. If the electric forces be regarded as the light vectors, the ratio of the intensities in the two glass prisms can be obtained from the ratio of the electric forces within the prisms. Neglecting losses due to absorption, and representing the component of the electric force perpendicular to the plane of incidence in the first and second prisms by E_s and D_s respectively, it has been shown that[2]

$$\frac{D_s^2}{E_s^2} = \frac{4\cos^2\varphi\left(\dfrac{\sin^2\varphi}{n_1^2} - 1\right)}{(1-n_1^2)(n_2^2-1)\sinh^2 u + (\cos\varphi + n_1 n_2 \cos\theta)^2\left(\dfrac{\sin^2\varphi}{n_1^2} - 1\right)}. \quad (1)$$

Here φ is the angle of incidence, within the first prism, on the boundary of the film; θ is the angle of refraction within the second prism; n_1, n_2 are the indices of refraction from the first prism into the film and from the film into the second prism respectively;

$$u = \frac{2\pi d}{n_1\lambda}\sqrt{\sin^2\varphi - n_1^2},$$

d being the thickness of the film and λ the wave-length of light within the film. The above equation expressing the ratio of the squares of the electric forces gives also the ratio of the squares of the amplitudes of the incident and emergent light. This will be the ratio of the intensities only when the two prisms have the same index of refraction. If n_1 is not numerically equal to $1/n_2$ the relative intensities will not be measured by the squares of the amplitudes merely, but the rates at which the energy is propagated by the corresponding waves in the two media must be taken into account. In this case, if the two media enclosing the film be different, the ratio of the intensities will be

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[1] PHYSICAL REVIEW, Vol. XV., p. 91.

[2] Loc. cit., p. 97.

$$\frac{D_s^2}{E_s^2} \tan \varphi \cot \theta = \frac{4 \cos^2 \varphi \left(\frac{\sin^2 \varphi}{n_1^2} - 1 \right) \tan \varphi \cot \theta}{(1 - n_1^2)(n_2^2 - 1) \sinh^2 u + (\cos \varphi + n_1 n_2 \cos \theta)^2 \left(\frac{\sin^2 \varphi}{n_1^2} - 1 \right)}. \tag{2}$$

If now the beam of light be reversed, φ and θ will interchange and $1/n_1$ replace n_2 and *vice versa*. Inserting these changes in (2) the ratio of the intensities within the two prisms becomes

$$\frac{D_s'^2}{E_s'^2} \tan \theta \cot \varphi = \frac{4 n_1^2 n_2^2 \cos \theta \, (n_2^2 \sin^2 \theta - 1) \tan \theta \cot \varphi}{(1 - n_1^2)(n_2^2 - 1) \sinh^2 u' + (n_1 n_2 \cos \theta + \cos \varphi)^2 (n_2^2 \sin^2 \theta - 1)}. \tag{3}$$

Since

$$n_2^2 \sin^2 \theta = \frac{\sin^2 \varphi}{n_1^2}$$

the second members of (2) and (3) may be reduced to an identity. It therefore follows that the penetration for any such system is the same whether the light passes from the denser to the rarer of the two media enclosing the film or in the reverse direction. Similar treatment yields the same conclusion for light polarized perpendicular to the plane of incidence. In the former discussion of the theory the factor tan φ cot θ was omitted and hence erroneous conclusions drawn.[1]

To test the conclusion under better experimental conditions than in the former measurements, a flint-glass prism, whose index of retraction for sodium light was 1.7597, was used with a crown-glass prism of refractive index 1.5164. The hypotenuse surface of the crown-glass prism was slightly convex. The prism angle for the flint-glass prism, 27° 54′, was such that when the two prisms were used in combination no deviation was obtained with sodium light. The source was a narrow yellow band from the spectrum of a Nernst lamp filament, the current being maintained practically constant by means of an electrodynamometer and an adjustable resistance. The following table gives the average of a number of closely agreeing readings. The light was polarized perpendicular to the plane of incidence; d is the depth of penetration in microns; i_1 and i_3, for the same line, are so related that i_3 is the angle of emergence from the flint-glass when i_1 is the angle of incidence on the crown-glass prism.

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[1] I am indebted to Professor Voigt for calling my attention to the error, by letter and also in Nach. d. K. Gesellschaft d Wissenchaften zu Gött. 1903 Heft 3 S. 1 where a different treatment yields the same conclusion.

Crown-glass, Air, Flint-glass.				Flint-glass, Air, Crown-glass.			
i_1	θ	d	d/λ	i_3	θ	d	$d \lambda$
5°	40° 42′ 20″	1.98	3.36	12° 30′ 00″	34° 58′ 45″	1.85	3.15
3	43 1 30	1.32	2.24	14 22 30	36 0 45	1.28	2.18
0	45 0 0	1.06	1.80	17 8 00	40 2 20	0.99	1.69

The differences in the values for the two cases are greater than the experimental errors. Repeated sets of measurements, taken with different intensities, all gave the same order of differences for the two cases. Light polarized parallel to the plane of incidence also gave the same result, the penetration is apparently greater when the light is incident on the crown-glass. The intensity observed, however, is not the intensity in the second prism but the intensity in air after the light has left the second prism, and futhermore it is the intensity in air before incidence on the first prism and not the intensity of the light incident on the film that is constant. The Fresnel coefficients for transmission from air to the first prism and from the second prism to air must be taken into account. The intensity of the light transmitted by the system for any given angle of incidence is not the same when the light is made to travel the same path, but in the reverse direction, unless the amount of light getting through the film varies directly as the intensity of the light incident on the film. This, however, is not the case, the penetration is a complicated function of the intensity.[1] For the condition under which the measurements were taken the results for the two directions therefore will not be identical. The penetration will be the greater for that direction in which the light incident on the film has the greater intensity. Using Fresnel's coefficient for light polarized perpendicular to the plane of incidence, the intensity of the light incident on the film when crown-glass is the first medium, for $i_1 = 5°$, is to the intensity of the light incident on the film when the flint-glass is the first medium, for the corresponding angle of incidence $i_3 = 12° 30'$, in the ratio of 959 to 929. Absorption has not been taken into account. Since the flint-glass has a distinct yellow tinge the losses due to absorption would increase rather than diminish the ratio of intensities as given. The greater value for the penetration obtained in the above table, when light was incident on the crown-glass, is thus accounted for, and it may be concluded that the penetration is independent of the order in which the light passes through the prisms.

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[1] Physical Review, Vol. XV, p. 100.

University of California,
Berkeley, July 5, 1905.

NEW BOOKS.

Maxwell's Theory and Wireless Telegraphy. Part I. by H. POINCARÉ. Part II. by FREDERICK K. VREELAND. 8vo, pp. xi + 255. New York, McGraw Publishing Co., 1904.

The first part of this book is a translation, by Mr. Vreeland, of Poincaré's "la Theorie de Maxwell et les Oscillations Hertziennes" which appeared in 1903 as one of the excellent "Scientia" series published by Naud. Beginning with an explanation of the essential features of the Maxwell theory, this portion of the book contains an account of electrical oscillations and electric waves considered from the scientific standpoint solely. The whole is written in the clear and pleasing style which characterizes all of Poincaré's writings.

The reader who knows Poincaré as a mathematician and mathematical physicist will perhaps be surprised at the complete absence of mathematical methods in the discussion. It is surprising also that so difficult a subject as Maxwell's theory can be so successfully presented without mathematical aid. M. Poincaré has given us another illustration of the significant fact that the greatest theoretical physicists have always been able to write clearly in ordinary language and in concrete terms. Every theoretical physicist must make frequent use of analytical methods: in the solution of problems as labor saving machinery, and in the statement of results as a convenient and useful shorthand. But the body is more than the raiment: a physical theory is more than the analytical expression with which we clothe it; and it is only the scientist of lesser caliber who is unable to separate the two.

M. Poincaré has made extensive use of mechanical analogies in helping to clear up difficult points. The translation here has a distinct advantage over the original in the fact that numerous illustrative diagrams have been inserted. The illustrations in the original were quite inadequate.

Wide differences of opinion exist regarding the benefit to be obtained from mechanical models in the study of electrical subjects. When the models are of such a character that the student thinks of them as actually representing the underlying mechanism of electrical phenomena, and proceeds to fill up space with an ether made up of cog wheels and spiral springs, I am inclined to agree with those who think that more harm than good is done by their employment. But M. Poincaré's models, and those introduced later by Mr. Vreeland, are not of that kind. Take for example the hydraulic analogy and the pendulum analogy, which are so effectively used in explaining the fundamental laws of electrical oscillations; or the mechanical models used by Vreeland later on in explaining the different methods of coupling the antenna to the primary vibrating system. There is not one reader in a thousand whose understanding of the subject will not be made clearer by the consideration of such mechanical parallels. Yet in all cases the model is so different from the reality that there is no danger of thinking of it as giving a picture of the actual processes. Such analogies as this are the parables of science; they convey as much in a sentence or a diagram as could be explained in several pages of exact statement.

After M. Poincaré's clear and adequate treatment of the scientific aspects of electric waves, we have in the second part of the book, by Mr. Vreeland, an almost equally satisfactory presentation of the principles of wireless telegraphy. The plan and scope of this part of the book are explained by a few sentences from the preface: "In Part II. it has been my purpose to take up the thread where M. Poincaré dropped it, carrying the line of thought into the practical field of wireless telegraphy, and applying the principles laid down in Part I. to the various problems involved; to describe certain typical systems, to show why some have failed while others succeeded, and to explain their mode of operation in the light of Maxwell's ideas. This is not intended as a treatise on wireless telegraphy — no attempt is made to describe the myriad forms of apparatus nor to settle questions of priority and history. * * * The object is rather to deal with principles and to trace the development of the art in its essential features."

Accounts of practical wireless telegraphy have been so often either highly technical or absurdly superficial that a treatment of the subject according to the plan outlined above is very welcome. The book contains no elaborate photographs of apparatus such as are often presented in our technical press as adequate illustrations of new systems: usually a confused jungle, in which induction coils and high tension transformers rise at intervals from an undergrowth of choke coils, relays, and sounders; the connections left to the imagination, and all really essential features concealed in camera-proof boxes. On the contrary the more important methods and systems are explained by the aid of simple diagrams of connections, and by reference to well chosen mechanical analogies. The essentials are there, and are explained in a sound and concrete way. Unessential details, which would only confuse the reader by their added complexity, are either left out of consideration altogether or are referred to only briefly. The author does not forget that he has set out to explain the *principles* of wireless telegraphy. In an art so new as this the forms of apparatus may change before a book describing them is off the press; but the underlying principles of telegraphy by electric waves will remain unchanged.

Mr. Vreeland's practical experience in wireless telegraph work gives him an advantage in preparing such a book that is often in evidence. What impresses me perhaps most as one of the results of practical experience is the manner in which the many difficulties which a careful reader would encounter are met and explained almost before they arise. It is evident in many cases that the author has met these difficulties himself in concrete form. Mr. Vreeland has wisely avoided discussion of the cases of disputed priority which are unfortunately so numerous. His references to the work of different inventors are fair and remarkably free from the bias that would be natural in one who has been intimately connected with one particular system out of the several competing ones.

The plan followed in Part II. is indicated by the following titles of chapters: General Principles; Telegraphy by Hertzian Waves; the Grounded Oscillator; Propagation of Grounded Waves; Receiving Apparatus; Selective Signaling. In the opinion of the reviewer the book is the most satisfactory that has yet appeared upon the subject of wireless telegraphy.

Ernest Merritt.

Volume XXI. *December, 1905.* *Numb*

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THE
PHYSICAL REVIEW

IONIZATION IN GASES FROM COLORED FLAMES.

By Percival Lewis.

Specific Velocity of Ions.

THE velocity of the ions in gases from the colorless bunsen flame was measured by McClelland.[1] His results (corrected for an obvious error in transforming from natural to ordinary logarithms) show specific ionic velocities of about 0.53, 0.48 and 0.09 cm./sec. volt/cm. in regions having temperatures of about 230°, 160° and 105° C., respectively. No one seems to have determined the velocity of the ions from flames colored with metallic salts.

It was found by the writer that the rate of discharge of an electroscope brought near a bunsen flame is reduced when a salt of any alkali metal is introduced into the flame. As the conductivity of the flame itself is greatly increased under such conditions, it seemed probable that the reduced conductivity of the hot gases could not be due to diminished ionization, but either to a much greater rate of recombination or to greatly reduced velocity of the ions. Some preliminary experiments showed the rate of recombination of the ions from the colored flame is not greater than that of the ions from the colorless flame, but that their velocity is very much less.

The velocity of the ions was measured by the method described by McClelland.[1] Above the flame was placed a long cylindrical brass chimney, 1.6 cm. in diameter (see Fig. 1), with a funnel-shaped opening at the bottom, to collect the hot gases. In the axis of the tube, at distances of 15 cm. from center to center, were suspended three cylindrical aluminum electrodes, *A*, *B* and *C*, each 12 cm. long and 6 mm. in diameter. These were insulated from the concentric brass chimney by small glass tubes passing horizontally through hard rubber plugs in the walls of the tube and containing the connecting wires. The outer cylinder and the flame were kept connected with the earth; any one of the electrodes could be connected with one pair of quadrants of a Dolezalek electrometer and charged by a battery of small storage cells giving a maximum potential of about 300 volts. The other quadrants were connected to earth. The lower electrode *A* was about 15 cm. above the flame. By means of a Gouy injector salt solutions were sprayed into a chamber through which the gas passed into the burner, carrying the spray with it.

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[1] McClelland, Phil. Mag., 46, p. 29, 1898.

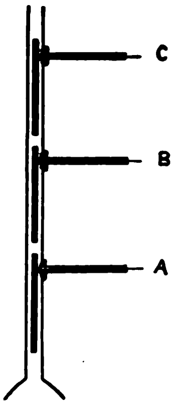

Fig. 1.

In making velocity determinations, the upper electrode *C* was first charged to such a high potential as to give a saturation current I_0 through the ionized gas between the electrode and the surrounding tube.[1] If the tube is at zero potential, the current will be carried solely by ions of sign opposite to that of the charge on the electrode. If N_0 be the total number of ions reaching the electrode per second and e the ionic charge, the current is

$$I_0 = N_0 e.$$

If, now, *B* is likewise charged with electricity of the same sign, the number of ions reaching *C* will be diminished by the number attracted to *B*, and the discharge current from *C* will be

$$I_1 = N_1 e.$$

If the difference of potential between the electrodes is V and the radii of the rod and the tube are r_0 and R respectively, the electric force at a distance r from the electrode is

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[1] See Rutherford, Radioactivity, p. 40.

$$X = \frac{V}{r \log_e \frac{R}{r_0}}.$$

If the specific ionic velocity is v, the radial velocity v_r at a distance r from the axis of the electrode is

$$v_r = Xv = \frac{Vv}{r \log_e \frac{R}{r_0}}.$$

The time required for the ions to reach the electrode is

$$t = \int_{r_0}^{r} \frac{dr}{v_r} = \int_{r_0}^{r} \frac{\log_e \frac{R}{r_0}}{Vv} r dr = \frac{\log_e \frac{R}{r_0}}{2Vv}(r^2 - r_0^2).$$

If l is the length of the electrode, only those ions will reach it which are not carried above it by the rising current in the time t, or which pass within the radius r. If u be the upward gas velocity, this time t is also

$$t = \frac{l}{u}.$$

From which

$$\frac{l}{u} = \frac{\log_e \frac{R}{r_0}}{2Vv}(r^2 - r_0^2),$$

$$v = \frac{u \log_e \frac{R}{r_0}}{2Vl}(r^2 - r_0^2).$$

If the ions are uniformly distributed through the cross-section of the tube,

$$\frac{I_1}{I_0} = \frac{N_1}{N_0} = \frac{R^2 - r^2}{R^2 - r_0^2}.$$

Therefore,

$$\frac{I_0 - I_1}{I_0} = \frac{r^2 - r_0^2}{R^2 - r^2} = \frac{d_0 - d_1}{d_0}.$$

d_0 and d_1 being the respective rates of discharge of the electrometer in scale divisions. From which we have,

$$r^2 - r_0^2 = \frac{d_0 - d_1}{d_0}(R^2 - r_0^2),$$

$$v = \frac{u \cdot \log_e \frac{R}{r_0}}{2Vl} \, \frac{(d_0 - d_1)}{d_0}(R^2 - r_0^2),$$

In this way the specific ionic velocity v of the ions as they pass B may be determined. The upward velocity u of the flame gases must be known to obtain exact values of v; but as it was soon found that the specific ionic velocity varies with the concentration of the solution in the flame, and as this is not capable of absolute determination, it seemed unnecessary to spend any time on the exact measurement of u. As a rough approximation, it was found that u was nearly 50 cm. per second, and this number was used in the calculations. The results are, therefore, not absolutely correct, but the relative values are probably fairly good.

The first measurements were made on the ions from the uncolored flame, at an average distance of about 30 cm. from the tip of the flame, around electrode B, where the temperature was about 150° The results were:

Velocity of positive ions	0.32 cm./sec.
Velocity of negative ions	0.33 cm./sec.

McClelland found that the velocity rapidly diminishes with the temperature, being 0.48 cm./sec. at 160° and only 0.09 at a temperature of 105°. The above results are consistent with those found by McClelland.

It was observed that these velocities were unchanged when either distilled or hydrant water was sprayed into the flame, showing that in the experiments described below the changes in velocity were not due to the water of the salt solution. It was also found that the gases from the colored flame were of about the same temperature as those from the uncolored, proving that the observed effects were not due to temperature changes.

Preliminary observations showed that the ions from the colorless flame move with much greater velocity than those from colored flames. In order, therefore, to prevent confusion resulting from a mixture of ions moving with different velocities, the swifter ions were removed by charging the electrode *A* to a few volts potential, sufficient to give a saturation current for these ions, while not appreciably disturbing the distribution of the slower ions.

As already stated, the ions from the colored flame move with velocities varying with the concentration of the solution. A systematic series of measurements was taken, using solutions of different concentrations of various salts of the alkali and calcium metals. It is evident from the observed effect of varying concentration that the velocity varies with the activity of the sprayer, as well as with variations in the height and temperature of the flame. In order, therefore, that observations taken on different days and under different conditions might be comparable, the initial and final observations in each series were made with a standard normal solution of NaCl, thus obtaining a factor to reduce results for other salts to the same relative scale.

The average velocities determined from a large number of readings with each solution are given in the accompanying table. Successive readings of rate of discharge, based on the time required for the spot of light from the electrometer mirror to pass over a given number of scale divisions, usually agreed within about 5 per cent.

Since the velocity varies with the concentration of the salt in the flame, which is an unknown quantity, it is evident that only the relative values have any significance.

The following conclusions may be derived from these figures:

1. The velocity of ions of the same sign from equimolecular (not chemically equivalent) solutions of all salts of all alkali metals is the same. This is also true of salts of the calcium group, but for these the velocities are less than two thirds those of the alkali group.

2. The velocity of the negative ions is in all cases somewhat greater than that of the positive. The ratio of these velocities is for all concentrations very nearly 1.13.

3. The specific ionic velocity varies inversely as the square root of the concentration of the salt in the flame, and consequently may vary with the activity of the sprayer with solutions of the same concentration. As shown in the table the product of velocity and square root of the concentration fluctuates about a mean value,

SPECIFIC VELOCITY OF IONS IN FLAME GASES (CM./SEC., VOLT/CM.).

Uncolored flame: + ions, 0.32; — ions, 0.33 (*at* 150° *C.*).
Colored flames:

Solution.	Saturated.		2 Normal.		*N*		½ *N*		¼ *N*		⅛ *N*		1/16 *N*		1/32 *N*		1/64 *N*	
	+	—	+	—	+	—	+	—	+	—	+	—	+	—	+	—	+	—
NaCl	.006	.007	.012	.012	.013	.013	.018	.023	.032	.034	.049	.052	.058	.061	.071	.090	.130	.140
NaI	8	8	12	13	15	16	......	......	33	36	......	......	53	63	......	......	......	.....
NaOH	7	9	......	......	.....	......	......	......	......	......	......	......	......	......	......	......	......	......
$NaNO_3$	5	7	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......
Na_2SO_4	.....	......	12	13	17	19	23	25	31	35	45	51	55	65	71	73	.130	.190
LiCl	5	5	......	......	......	......	......	......	......	......	......	.....	......	......	......	......	......	......
LiBr	......	......	13	13	16	16	21	24	33	39	49	60	70	80	......	......	......	......
KI	......	......	11	12	16	20	......	......	26	27	......	......	60	75	90	95	.160	.180
RbCl	......	......	......	......	......	......	......	......	30	34	46	50	70	80	82	100	.120	.140
Average v.	.006	.007	.012	.013	.015	.017	.021	.024	.031	034	.047	.053	.060	.071	.079	.089	.135	.162
$v \times \sqrt{\text{conc.}}$ +	......	......	168	......	150	......	147	......	155	......	167	......	153	......	143	......	169	......
$v \times \sqrt{\text{conc.}}$ —	......	......	.....	180	......	170	......	168	......	170	......	189	......	178	......	156	......	200
$Mg(NO_3)_2$	......	......	......	.....	9	11	......	......	21	......	......	......	28	......	......	......	......	......
$CaCl_2$	......	......	......	......	10	11	14	17	19	20	......	......	35	36	......	......	......	......
$Sr(NO_3)_2$	......	......	......	......	10	12	......	......	16	17	......	.....	33	36	......	......	......	......
$BaBr_2$	......	......	......	......	8	10	......	......	16	19	.....	......	27	29	......	......	......	......
Average v.	......	......	......	......	.009	.011	.014	.017	.017	.019	......	......	.031	.034	......	......	......	......
$v \times \sqrt{\text{conc.}}$ +	......	......	......	......	90	......	98	......	85	......	......	......	78	......	......	......	......	......
$v \times \sqrt{\text{conc.}}$ —	......	......	......	......	......	110	......	119	......	95	......	......	......	85	......	......	......	.....

differing from it by as much as 10 per cent. only in two or three cases.

The diminished velocity of the ions as the temperature falls or with the lapse of time is usually attributed to the formation of molecular aggregates about the original ions as nuclei, as illustrated in the condensation of water vapor on ions. If this is the explanation of the observed changes in velocity with changes in concentration, it would appear that ions from colored flames do not tend to form aggregates with the molecules of the surrounding atmospheric or flame gases or water vapor, but only with molecules of their own or similar kind. That they may form aggregates with molecules of a similar kind is shown by the fact that when a normal solution of a sodium salt is added to a normal solution of a potassium salt no change in ionic velocity is observed, although the sodium salt or the potassium salt solution *per se* is reduced thereby to half its original concentration.

As shown by the experiments of Townsend and of Langevin and in accordance with the theoretical deductions of J. J. Thomson,[1] the coefficients of diffusion and the velocities of the ions in a given gas are inversely proportional to the pressure of that gas. The changes of velocity here described, however, are not due to variations of the total pressure; they would be inversely proportional to the partial pressure of the ions concerned if we assume that ionization is proportional to the square root of the concentration. Townsend has shown, however, that the coefficients of diffusion of the ions produced in any gas by the action of Röntgen rays, Becquerel rays, and ultra-violet light are the same; and Zeleny, Rutherford and Chattock[2] have shown that the velocities of the ions produced by Röntgen rays, ultra-violet light, and the spark discharge are the same; and yet in these several cases the degree of ionization was probably very different. It does not appear to be generally true, therefore, that ionic velocities are inversely proportional to the partial pressure of the ions. That it appears to be so in this case may perhaps be explained as follows:

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[1] Thomson, Cond. Elect. through Gases, p. 30; Townsend, Phil. Trans., 195, 259, 1900; Langevin, Paris Thesis, 1902.

[2] Rutherford, Proc. Cam. Soc., 14, p. 401, 1898. Zeleny, Phil. Trans., 195, p. 193, 1900. Chattock, Phil. Mag., 46, p. 401, 1897.

Free diffusion of different gases takes place at a rate very nearly inversely as the square root of their molecular weights. As found by Townsend,[1] the coefficients of ionic diffusion in various gases are also roughly in the same proportion. Measurements of the specific ionic velocities in various gases, made by Rutherford, Zeleny, Chattock, and others, show that these velocities vary approximately, according to the same law. There is, then, empirical evidence that, other things being equal, the mobility of either molecules or ions under the action of any forces acting on them is very nearly inversely proportional to the square root of their mass. The same may be assumed to be true of molecular aggregates. If, then, an ion collects around it aggregates of molecules of its own kind, at every collision it will pick up a new molecule. The number of collisions, and therefore its mass after a given length of time, will be proportional to the concentration of those molecules. Hence it would follow that the ionic velocity will vary inversely as the square root of the concentration of molecules of the kind from which the ions originated.

It appears that changes of velocity with concentration have not been previously noted except by Moreau,[2] who found that in the bunsen flame the velocity of negative ions of the alkali metals increases with diminishing concentration, but not so rapidly as is the case in the flame gases; and that at a given concentration the velocity in the flame varies inversely as the square root of the atomic weight of the metal.

It remains to be explained why the ions of all salts of all similar metals move in the flame gases with the same velocity, without regard to great differences of the atomic weights concerned. As shown by others, this is also true of ions within the flame. It is possible that in all these cases we are not dealing directly with the different elements, but rather with secondary products of reactions in the flame, which are the same in every case.

Various comparisons of the saturation currents in the gases from the colorless flame with those in gases from flames into which normal solutions were sprayed, showed that in the latter case the currents were from ten to twenty times as great as in the former, the ratio varying with the distance from the flame. Since, however, the velocity of the ions from the colored flame is only about one fiftieth that of the other kind, the unsaturated current, dependent upon velocity of ions as well as upon degree of ionization, and expressed thus,

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[1] Townsend, Phil. Trans., 193, p. 127, 1901.

[2] Moreau, Jl. de Physique, 2, p. 556, 1903.

$$i = Ne(v_+ + v_-)X,$$

may be much less in the case of the colored flame. Thus the observations of the apparently decreased conductivity of the colored flame gases which led to this investigation are explained. It is also evident that, if we take account of the variation of velocity with concentration in the flame itself, as found by Moreau, we cannot determine the degree of ionization by conductivity experiments with small electromotive forces, but should in every case base conclusions only on saturation currents.

Comparison with the results obtained by H. A. Wilson[1] shows the following changes of velocity with temperature:

	+	−
In flame at 2000° (Wilson)..............	62	1000
In heated tube at 1000° (Wilson).. ...	7.2	26
In flame gases at 150° (Lewis).........	.006	.007

Wilson found that in the case of ions from solutions of calcium salts sprayed into a tube at 1000° the velocity of the positive ions was only 3.8 as compared with 7.6 for the alkali metals — a proportion very nearly the same as that found in these experiments.

These figures illustrate the rapid formation of aggregates as the temperature falls, with the resultant diminution in the difference between the velocities of the positive and the negative ions. J. J. Thomson has suggested that the smaller velocities of ions from the calcium group found by Wilson indicates that bivalent ions form larger molecular complexes.

RATE OF RECOMBINATION.

One of the aluminum electrodes previously used was suspended inside a long brass tube 1.6 cm. in diameter by a fine insulated wire connected with the electrometer and charged by the battery. By placing this electrode at different distances from the flame and noting the rate of discharge the rate of recombination was determined.

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[1] H. A. Wilson, Phil. Trans., 192, p. 499, 1899.

The saturation currents at different distances from the flame were proportional to the following numbers:

Distance from Flame.	20	25	30	35	40	45
Colorless flame.	40	21	11	8	6	4
NaCl normal.	100	74	60	52	44	40
$\frac{1}{4}$ normal.	75	60	44	38	34	32
$\frac{1}{16}$ normal.	66	56	40	36	32	28

These results are shown graphically in Fig. 2.

From these figures it appears that the rate of recombination of the gases from the colorless flame is much greater than that of the gases from the colored flame. The latter rise 15 cm. in the tube before the ionization is reduced to one half its original amount, while the gases from the former become half recombined in rising 5 cm. Changes in concentration do not appreciably affect the gradient of the recombination curve for the gases from the colored flame. If the ionization in the gas is proportional to that in the flame, if the ionization in the latter is directly proportional to the square root of the concentration, as the experiments of Arrhenius

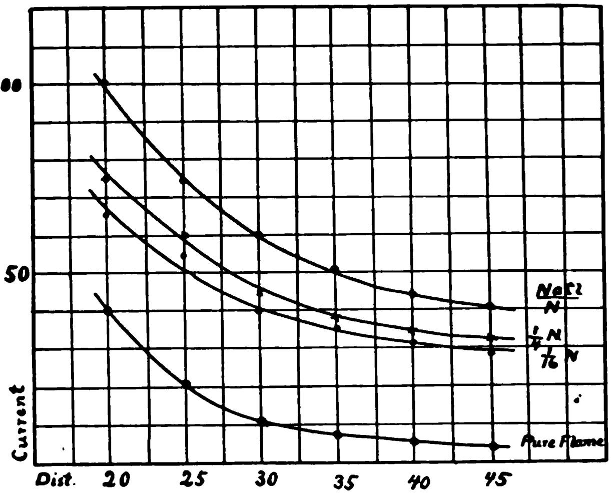

Fig. 2.

and others indicate, and if the velocity varies inversely as the square root of the concentration, no change in the rate of recombination with concentration should be expected; for this rate must be proportional to the product of number and velocity of ions present.

Further tests were made to find how the ionization in the flame-gases varies with the concentration of the solution used.

Relation Between Concentration and Conductivity.

With an arrangement similar to that used in determining the rate of recombination, the saturation current was measured in two regions at an average distance of 20 and 60 cm., respectively, from the flame, with an electrode 12 cm. long; and as a further guarantee that the saturation should be complete, a third set of measurements was made with an electrode 25 cm. long at an average distance of 40 cm. from the flame. The currents observed were proportional to the following numbers:

Distance.	Electrode 12 cm. Long.		Electrode 25 cm. Long
	20 cm.	60 cm.	40 cm.
Colorless flame.	33	3.5	11
NaCl $\frac{1}{256}$ normal.	35	11	28
$\frac{1}{64}$ "	44	15	35
$\frac{1}{16}$ "	53	18	41
$\frac{1}{4}$ "	70	24	60
1 "	100	32	79

It appears, therefore, that the ionization increases rapidly with the concentration, but not in a proportion lying between the square root and the first power of the concentration, as appears to be the case within the flame.[1] The proportion is, in fact, more nearly as the fourth root. Nevertheless, these results favor the view that the ionization within the flame is in part at least a volume effect, not purely a surface effect at the electrodes; for in this case no electrodes in the flame were used, and yet great increase in ionization accompanied increase in concentration; and increased ionization in the flame-gases suggests increased ionization in the flame itself.

At 20 cm. from the flame it is to be seen from the above figures that the saturation current is very nearly as great through gases from the colorless flame as through those from a flame sprayed with $\frac{1}{256}$ normal NaCl solution, and one third as great as when the solution is normal, although further away it is much less. This may in part be due to the fact that, on account of the great velocity of ions of the first kind near the flame, many ions are drawn up to the electrode from the flame itself as well as from the space between the electrodes, while this would not be true to the same extent of the slower-moving salt ions. Further observations indicated, however, that this can hardly be the complete explanation, and that in reality the total ionization within the colored flame may not be greatly different from that in the pure flame, provided that the electrodes are not within the flame.

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[1] J. J. Thomson, Cond. of Elect. Through Gases, p. 200.

TOTAL IONIZATION AT THE BOUNDARIES OF THE FLAME.

Two rectangular electrodes were made out of sheet iron about 25 by 30 cm., with a cylindrical depression hammered into each in such a way that when they were placed vertically and parallel to each other at a distance of about one cm. there was a central cylindrical enlargement containing the flame. By this arrangement the electrodes almost completely surrounded the flame and had a large enough surface to insure a saturation current with a potential difference of 250 volts. The currents observed were beyond the range of the electrometer, and a sensitive galvanometer was used instead. Some observations were made with the electrodes as near as possible to the flame without actually touching it, and others at varying distances up to about 5 cm. apart. In all cases the ions were completely collected by the electrodes, as shown by the fact that a charged electroscope held immediately above the flame was not discharged while the current was flowing. Below is given a series of galvanometer deflections in millimeters, with the electrodes at different distances.

Pure Flame.	Flame Sprayed with Saturated NaCl Sol.
8	17
9	13
9	14
4	6
3	5
3	6
2	3
38	64

The rather remarkable fact seems demonstrated by these figures that there issue from the flame charged with saturated NaCl solution spray less than twice as many ions as from the pure flame, in spite of the well-known fact that when the electrodes are inserted in the flame the conductivity is greatly increased by the spray. It must be inferred, therefore, that the far greater ionization in the gases from the colored flame at a distance from the latter is not due to the fact that the initial ionization was greater in the same proportion, but rather to the fact that the ions in one case disappear by recombination, and in the other persist because of slower rate of recombination.

It was found that a saturated solution of KI gave about three times as much current as the pure flame. This is in accordance with the well known fact that in the flame potassium salts are better conductors than sodium salts.

Similar results were obtained by H. A. Wilson.[1]

These results (assuming proportionality between ionization inside the flame and that just outside of it) tend to confirm the view of J. J. Thomson and H. A. Wilson that the great conductivity of colored flames is principally due to the incandescent electrodes, particularly the cathode.[2]

It is stated by Wilson (*loc. cit.*) that an earthed strip of incandescent platinum between electrodes just outside the flame greatly increased the conductivity. It was found, however, that the introduction of incandescent platinum or carbon in the flame produced no noticeable increase in the conductivity of the flame gases.

These experiments are not wholly free from contradictory features. As we do not know that ionization within the flame and that just outside of it are strictly the same in character and proportional to each other, they do not determine whether the ionization within the flame is a volume or surface effect; but the most consistent interpretation seems to be that there is a volume ionization in colored flames somewhat though not greatly in excess of that in uncolored flames; that the part of the ionization due to the salt solution varies with the concentration of the solution, in a proportion lying between the fourth root and the square root of the concentration; and that the conductivity of the flame is greatly increased by the insertion of the electrodes into the flame.

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[1] H. A. Wilson, Phil. Trans., 192, 510, 1899.

[2] *Note added Oct. 18, 1905:* Some results just obtained by Mr. J. G. Davidson in this laboratory indicate that the difference of conductivity is due to the position of the electrodes in the flame, but not to their temperature.

UNIVERSITY OF CALIFORNIA,
September 8, 1905.

EXPERIMENTS ON RESONANCE IN WIRELESS TELEGRAPH CIRCUITS. PART III.

By George W. Pierce.

THE experiments here described, like those of the earlier papers,[1] deal with the resonance conditions in wireless telegraph circuits of the *electromagnetically connected type*. A diagram of this type of circuits is shown in Fig. 24. *S* represents the sending station, *R* the receiving station. The two stations are 187 meters apart. A form of high-frequency dynamometer in Circuit IV. at the receiving station serves to measure the energy transmitted to the receiving station by the electric waves.

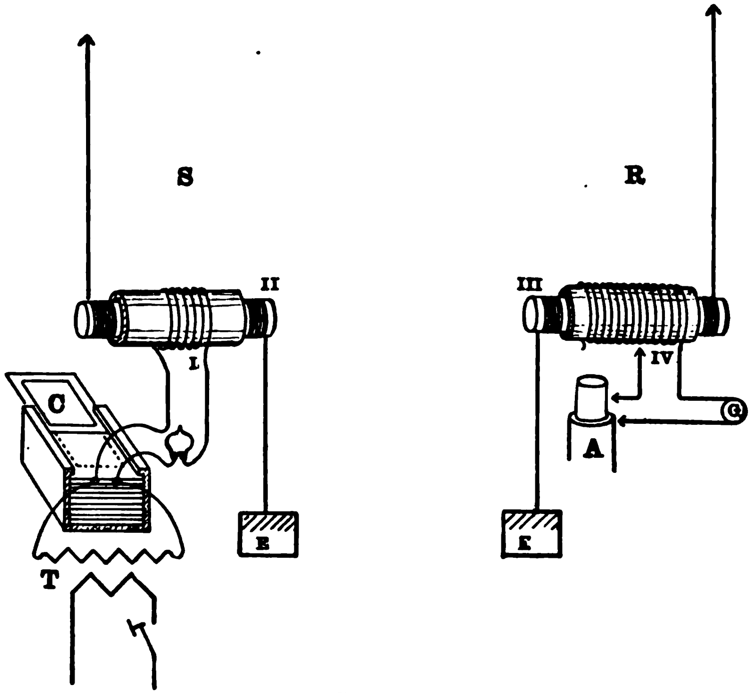

Fig. 24.

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[1] Parts I. and II. were published in Vol. XIX., September, 1904, and Vol. XX., April, 1905, of the Physical Review.

In the previous experiments the capacities C and A, the coils I., II., III., IV., and the form and height of the antennæ at the two stations have been varied. Empirical formulas for the resonant relation of these several quantities were obtained, and these formulas were found to be in fair agreement with theoretical deductions.

In the present experiments it is proposed to investigate the effect of varying the mutual inductance between the two circuits at each station,— that is, the effect of varying the *coefficient of coupling*.

The coefficient of coupling τ is defined for the two stations by the equations,

$$\tau_1 = \frac{M_{12}}{\sqrt{L_1 L_2}}, \quad \tau_2 = \frac{M_{34}}{\sqrt{L_3 L_4}}.$$

The importance of these coefficients of coupling in determining the sharpness of resonance and strength of signals has been pointed out by M. Wien.[1] From theoretical considerations he shows that when τ is large at the two stations, waves of great intensity are transmitted, and stations with large values of τ are adapted to signalling to great distances. Under these conditions, however, that is, with large values of τ, the resonance is not sharp, and may be no sharper than with the simple system in which spark-gap and receiving instrument are placed directly in the mast circuits.

On the other hand, when τ is small at both stations the resonance is sharp, though the distance that may be covered is not great.

A system of wireless telegraphy with large value of the coefficient of coupling is called by Wien a "close coupled" system, while a system with a small value of τ is called "loose coupled." The loose coupled system of sending and receiving stations should give the sharp resonance. These several propositions are here submitted to experiment.

IX. RESONANCE EXPERIMENTS WITH VARIATION OF THE COEFFICIENT OF COUPLING.

Experiment X. Resonance curves with variation of coefficient of coupling and height of antenna at the receiving station. — The coils employed in the four circuits had the following values:

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[1] D. A., Vol. VIII., p. 686, 1902.

Coil No.	No. of Turns.	Diameter of Wire, cm.	Length of Solenoid, cm.	Inductance, Henries.
I.	9	.164		1.71×10^{-5}
II.	240	.104	46	125×10^{-5}
III.	240	.104	46	125×10^{-5}
IV.[1]	17	.164		7.04×10^{-5}

Mutual Inductances.—The mutual inductance between Circuits I. and II. at the *sending station* was left constant. The value of this mutual inductance was

$$M_{12} = 4.90 \times 10^{-5} \text{ henries.}$$

The coefficient of coupling at the sending station was, therefore,

$$\tau_1 = \frac{M_{12}}{\sqrt{L_1 L_2}} = \frac{4.90}{\sqrt{125 \times 1.71}} = .335.$$

The mutual inductance between Coils III. and IV., and, therefore, the coefficient of coupling at the *receiving station*, was varied by displacing the inner coil, III., in the direction of its axis, while the outer coil, IV., was left stationary. The value of the mutual inductance for several relative positions of the two coils was known from a comparison with an earth inductor. Experiments were made with the following values of the mutual inductance and coefficient of coupling at the receiving station :

M_{34}. Henries.	τ_2	τ_2^2
8.9×10^{-5}	.30	.090
6.4×10^{-5}	.213	.047
4.17×10^{-5}	.141	.020
2.12×10^{-5}	.071	.0051

From the theory it is known that τ_2 enters in the resonance condition only as τ_2^2, which comes into the equations usually in comparison with unity. The present experiments then cover a range of values of τ_2^2 from 9 per cent. to ½ per cent. of unity.

The process of the experiment was as follows : First, the condenser in the side circuit at the sending station was adjusted so that the sending station gave out waves of a definite wave-length as free from harmonics and distortions as was possible with the condition of coupling that prevailed at the sending station. This was done, as described in the previous papers, by taking a series of resonance curves in the following manner. With the sending and receiving antennæ of the same dimensions, namely, a single wire 16 meters long, resonance curves at the receiving station were taken for several values of condenser capacity at the sending station. These curves are shown in Fig. 25. The different curves correspond to different values of the condenser at the sending station, and the individual points of each curve are the deflections obtained with various values of capacity of the air condenser at the receiving station. The details of the method of obtaining these curves are given in Part I.

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[1] Including the instrument.

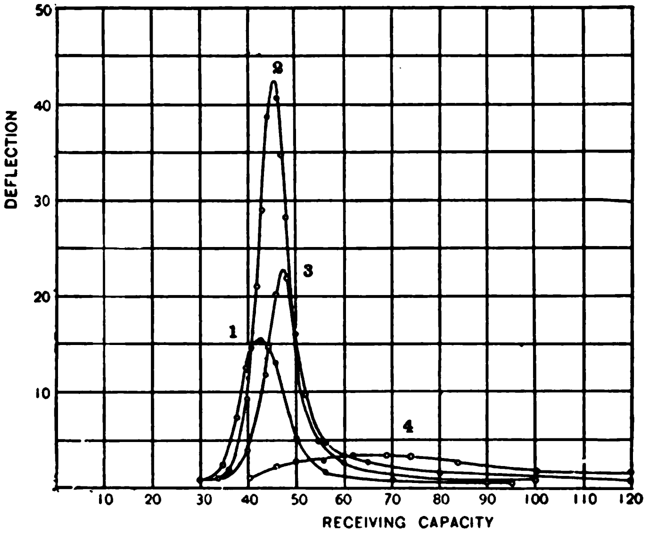


Fig. 25.

Curve 2 shows the best resonance, and the capacity in the sending side circuit was set at the value that gave curve 2 and kept at that value throughout the remaining steps of the experiment.

The antenna at the sending station (16 meters of single wire) was also left unchanged.

Thus with a source of waves of constant wave-length and approximately constant intensity, variations were made at the receiving station, and the effects of the variations were studied by means of the deflections obtained in the high frequency dynamometer.

The variables at the receiving station were the height of antenna, the coefficient of coupling, the capacity of the air condenser *A*, Fig. 24, and the deflections.

The receiving antenna consisted of various heights of two parallel wires .208 cm. in diameter and 57 cm. apart.

For a particular height of antenna, 24 meters, and a particular value of τ_2 ($\tau_2 = .30$) the curve marked 24 in Fig. 26 was obtained. In this curve the deflections of the receiving instrument are plotted against centimeters of length of the air condensers in the receiving side circuits — each centimeter of the condenser being 2.77×10^{-11} farads.

Other heights of the receiving antenna, *e. g.*, 18, 14, 10 and 9 meters, gave the curves marked 18, 14, 10 and 9 in Fig. 26. These curves and many others corresponding to other heights of antenna were taken with the same value of τ_2, $\tau_2 = .30$.

So far the experiment is exactly analogous to several experiments described in more detail in Part II. As in the previous paper, by an examination of the curves of Fig. 26 it is seen that as the length of receiving antenna is decreased it is necessary to increase the capacity of the air condenser in the side circuit to obtain resonance. The exact relation between this height of antenna and the resonant capacity in the side circuit at the receiving station is represented in curve *FF′* of Fig. 27, in which height of antenna is plotted against resonant capacity in the side circuit. The curve *FF′* as was pointed out in Part II. is approximately the two branches of a hyperbola.

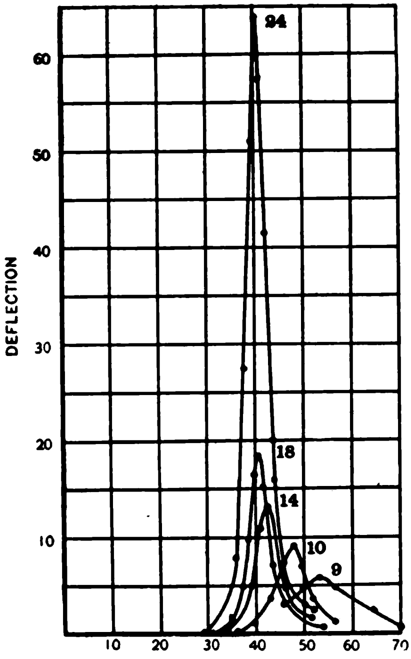


Fig. 26.

Variation of τ_2.—Along with the curves of the family ($\tau_2 = .30$) represented in Fig. 26, similar curves were taken with other values of the coefficient of coupling at the receiving station; namely, with τ_2 equal .213, .141, .071. This gives three other families of curves similar to the partial family in Fig. 26. The drawings of the individual curves of the three new families are not here given, but it is attempted to present the results obtained by a discussion of the data with respect to the effect of τ_2 on the capacity hyperbola, effect of τ_2 on energy received with various heights of antenna, and effect of τ_2 on sharpness of resonance.

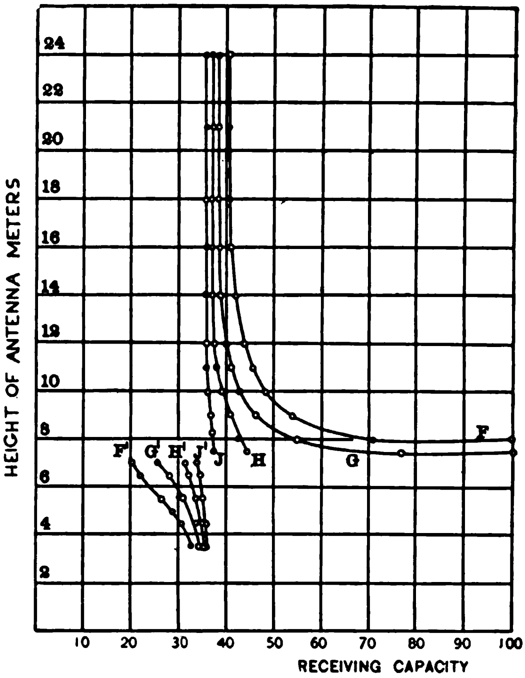


Fig. 27.

1. *With respect to the capacity hyperbola* reference is again made to Fig. 27. The approximate hyperbola *FF'* represents the relation between the height of antenna and the capacity C_4 in the side circuit at resonance. When the value of the coefficient of coupling is diminished from $\tau_2 = .30$ to the values $\tau_2 = .213$, .141 and .071, the above relation takes the form of the curves *GG'*, *HH'* and *JJ'*,

respectively. That is the approximate hyperbolas move in towards their asymptotes and approach coincidence with the vertical asymptote. Also the asymptotes shift slightly toward the origin of coördinates.

This result might have been predicted from the theoretical equations given in Part II. It was there shown that for a given frequency of incident waves the condition for resonance between the two parts of the receiving circuit is expressed as a first approximation by the equation,

$$\left(C_3 - \frac{L_4}{a\omega^2}\right)\left(C_4 - \frac{L_3}{a\omega^2}\right) = \frac{M^2}{a^2\omega^4}, \tag{1}$$

in which C_3 is the capacity of the mast circuit, C_4 the capacity of the side circuit coupled with it, L_3 and L_4 the self inductances of the two circuits, M the mutual inductance of these two circuits, ω the angular velocity of the incident waves, and

$$a = L_3L_4 - M^2 = (1 - \tau_2^2)L_3L_4. \tag{2}$$

Equation (1) is the equation of a hyperbola with asymptotes $C_3 = L_4/a\omega^2$ and $C_4 = L_3/a\omega^2$.

In the curves of Fig. 27, instead of the capacity of the antenna, we have the height of the antenna, which the previous experiments showed to be approximately proportional to its capacity. For a given change of τ_2 the displacement of the asymptotes in the experimental hyperbola would, therefore, be proportional to the displacement of the asymptotes of the theoretical hyperbola. The effect of diminishing τ_2 in the theoretical equation is seen to be a slight shifting of the asymptotes toward the origin and an approaching of the curves toward their vertical asymptote — an effect that is plainly apparent in the experimental curves.

Numerical Test. — To ascertain whether the four curves of Fig. 27 are in agreement with the elementary theory given in Part II., they are here examined numerically. The curve FF' is approximately represented by the equation

$$(H_f - 7.1)(C_4 - 39) = 25. \tag{f}$$

In the experiment by which this curve was obtained τ_2 was .30.

The constants of equation (f) when changed appropriately for the change in τ_2 should give the constants of the equations to the curves GG', HH' and JJ'. The way to make these changes is apparent from equation (1). For example, the constant to be subtracted from height of antenna is inversely proportional to $(1 - \tau_2^2)$, the constant to be subtracted from C_4 is also inversely proportional to $(1 - \tau_2^2)$, while the constant on the right hand side of the equation is proportional to τ_2^2 and inversely proportional to $(1 - \tau_2^2)^2$. Making the changes suggested by these relations we derive the following equations for the curves GG', HH' and JJ':

$$(H_g - 6.8)(C_4 - 37.2) = 11.5 \qquad (g)$$
$$(H_h - 6.6)(C_4 - 36.2) = 4.75 \qquad (h)$$
$$(H_j - 6.3)(C_4 - 36.0) = 1.16. \qquad (j)$$

The equations (g), (h) and (j) do not represent the curves GG', HH' and JJ' of Fig. 27 as well as the equations (g'), (h') and (j'), p. 375, in which the values subtracted from the height of antenna are 7.2, 7.0 and 7.0, instead of the values 6.8, 6.6 and 6.3 in the theoretical equations.

TABLE XVI.

Relation Between Height of Receiving Antenna and Resonant Capacity, with Variation of τ_2.

Meters Antenna Above Coil, H	$\tau_2 = .30$.		$\tau_2 = .213$.	
	Resonant Capacity Observed, C_4	Resonant Capacity Calculated.	Resonant Capacity Observed, C_4	Resonant Capacity Calculated.
24	40.5	40.4	38.5	37.9
21	40.5	40.5	38.0	38
18	41.0	41.4	38	38.3
16	41	41.7	38.5	38.5
14	42	42.6	39	38.9
12	44	44.1	40	39.4
11	45.5	45.4	41	40.6
10	47	47.6	42.5	41.7
9	54	52	46.3	43.7
8	71	67	55	53.3
7.5	100	101	77	78.2
6.5	22	—	28	4.0
5.5	27	23.4	31	13
4.5	30.5	29.4	33.5	28
3.5	33	32	34	31

$$(H_g - 7.2)(C_4 - 37.2) = 11.5 \qquad (g')$$
$$(H_h - 7.0)(C_4 - 36.2) = 4.75 \qquad (h')$$
$$(H_j - 7.0)(C_4 - 36.0) = 1.16. \qquad (j')$$

This departure is slightly larger than could arise in error of measurement. With decrease of τ_2 the horizontal axis of the curves does not move downward as much as the theoretical equation (1) requires. This discrepancy, together with the departure of curves like *FF'*, *GG'*, *HH'* and *JJ'* from true hyperbolas, probably arises in the assumption made in Part II. that cutting off wire from the antenna does not change the self inductance of the mast circuit by an amount significant in comparison with the inductance of the coil in the mast circuit. That is, in the theoretical discussion of the resonance conditions (Part II.), the capacity of the antenna was supposed to be localized instead of distributed. The present experiment shows that this supposition enables us to predict approximately the shape and interrelation of the curves of Fig. 27, but that when submitted to strict test a slight departure between theoretical and experimental values is detected.

TABLE XVII.

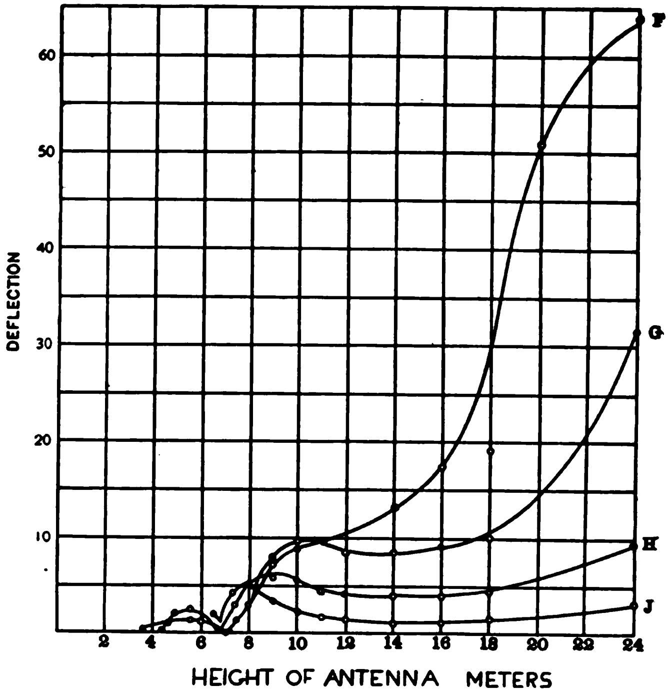
Relation between Height of Antenna and Resonant Capacity with Variation of τ_2.

Meters Antenna Above Coil, H.	$\tau_2 = .141$.		$\tau_2 = .071$.	
	Resonant Capacity Observed, C_4.	Resonant Capacity Calculated.	Resonant Capacity Observed, C_4.	Resonant Capacity Calculated.
24	37	36.5	36	36.1
21	37	36.5	36	36.1
18	37	36.6	36	36.1
16	37	36.7	36	36.1
14	37	36.9	36	36.2
12	37.5	37.2	36	36.2
11	38	37.3	36	36.3
10	39	37.6	36.5	36.4
9	41.2	38.4	37	36.6
8	42.5	40.7	37	36.7
7.5	45	45.7	37.5	38.2
7	32	—	34	—
6.5	32	26.7	35	33.7
5.5	34.1	33.1	35.5	35.3
4.5	35	34.3	36	35.5
3.5	36	34.9	36	35.7

Tables XVI. and XVII. give the observed values of resonant condenser capacity corresponding to various heights of receiving antenna in comparison with the values calculated from equations (f), (g'), (h') and (j').

2. *With respect to the effect of τ_2 on the energy received with various heights of antenna*, reference is made to Fig. 28. In this figure the deflection of the instrument, that is, the square of the current in the instrument circuit, is plotted against the height of receiving antenna for various values of τ_2. The deflections are the readings of the dynamometer when the condenser circuit and the mast circuit at the receiving station are in resonance. They were taken with different values of the sensitiveness of the receiving in-

Fig. 28.



Curves showing energy received with various heights of antenna and various values of the coefficient of coupling at the receiving station. The deflections were taken with the condenser circuit in resonance with the mast circuit. Each point in the present figure is thus the vertex of a resonance curve from Fig. 26 or from a similar family. Curve F, $\tau_2 = .30$; Curve G, $\tau_2 = .213$; Curve H, $\tau_2 = .141$; Curve J, $\tau_2 = .071$.

strument but they are all reduced to the same scale, namely the deflection of the instrument in centimeters at one tenth its best sensitiveness.

Table XVIII. is given to show numerically the relative values of the deflections. These measurements were taken in a series extending over several days and are subject to errors arising from change of interrupter, change of weather, and change of the instrument due to expansion of the vulcanite mounting of the coil, and are hence not as accurate as observations taken in a short series, like that of determining a single resonance curve.

Table XVIII.

Effect of τ_2 on Energy Received.

τ_2	.30	.213	.141	.071
Ratio, $\tau_2/.30$	1	.72	.47	.24
Ratio Squared.	1	.52	.22	.056
Height Meters.	**Relative Deflection.**			
24	1	.48	.142	.048
18	1	.59	.26	.068
16	1	.60	.255	.076
14	1	.66	.30	.087
12	1	.80	.39	.122
11	1	.88	.39	.158
10	1	.97	.63	.23
9	1	1.03	.93	.49
8	1	1.05	1.52	1.94
7.5	1	.80	1.37	3.0
7	1	3.9	8.0	14.2

Table XVIII. shows that when the antenna is long the deflections are roughly proportional to τ_2^2. Since the deflections are proportional to the square of the current in circuit IV. and τ_2^2 is proportional to the square of M_{34}, this relation is of the order that one should expect. When the height of the antenna is diminished the ratio of the deflections varies in a complex manner, on account of the occurrence of a maximum and a minimum at different heights of antenna in the four cases.

3. *With respect to the effect of τ_2 on the sharpness of resonance* Fig. 29 shows two characteristic curves, one taken from the set with $\tau_2 = .30$, the other from the set with $\tau_2 = .071$. For both

curves the height of antenna was 24 meters. In Fig. 29 deflection is plotted against percentage departure of capacity from resonant capacity. The deflections observed for the dotted curve ($\tau_2 = .071$) are about one twentieth the deflections for the heavy-line curve ($\tau_2 = .30$), but in the figure the maximum deflection of each is called 100 so that it may be seen how the deflections fall away from the maximum deflection with change of capacity from resonant capacity.

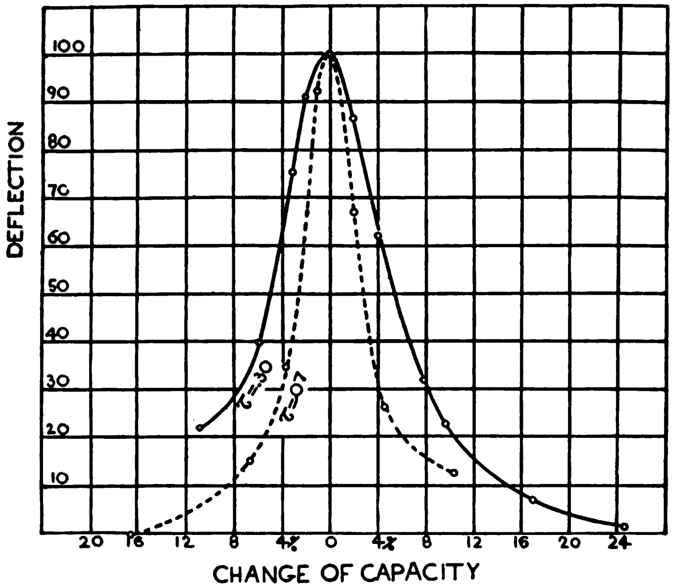


Fig. 29.

With $\tau_2 = .30$ the deflection falls to half for a change of capacity of about 5 per cent., while with $\tau_2 = .071$ the deflection falls to half for a change of capacity of 2.5 per cent. The deflection is proportional to the energy and the capacity proportional to the square of the period, so we may say that the energy received falls to half for a dissonance of 2.5 per cent. and 1.25 per cent. in the two cases respectively.

For the cases in which τ_2 had intermediate values between .30 and .071 the curves of energy against dissonance lie between the two curves plotted in Fig. 29.

Experiment X. thus confirms the theoretical deduction that with decrease of the coefficient of coupling the sharpness of resonance is increased. The gain in sharpness of resonance is, however, paid for by a loss in energy. For with constant sending station in order to improve the sharpness of resonance two-fold, it was necessary to change the coefficient of coupling at the receiving station to such an extent that the energy received was decreased twenty-fold. Of course these particular numbers hold only when the receiving instrument has a very low resistance. In these experiments the resistance of the dynamometer was only 1.33 ohms. With a high resistance receiving instrument it is not possible to obtain resonance as sharp as that here found, and the effect in sharpness of resonance produced by diminishing τ would be less than in the case under observation. I have been taking some data with the electrolytic and mychrophonic receivers but the experiments are not yet ready for presentation.

Experiment XI. With Decrease of Coefficient of Coupling at the Sending Station. — The coefficient of coupling was decreased at the sending station without appreciable gain in the sharpness of resonance. This result may be due to the fact that with the condensers employed at the sending station in the present experiments the changes of capacity were made step-wise, and possibly the steps were not small enough to afford the proper adjustments when the coefficient of coupling at the sending station was small.

Wave-length. — The wave-length of the sending station in the present experiment may be calculated from the position of the vertical asymptote of any one of the curves FF', GG', HH' and JJ', of Fig. 27, by the aid of the equation

$$C_4 = \frac{L_3}{a\omega^2} = \frac{1}{(1 - \tau_2^2)L_4\omega^2} \tag{3}$$

in which C_4 is the abscissa of the vertical asymptote. The wave-length is obtained by determining ω from Equation 3. The computation is very simple if use is made of the curve JJ', for in that case τ_2^2 is negligible, and we have, remembering that each centimeter of the air condenser equals 2.77×10^{11} farads,

$$36 \times 2.77 \times 10^{-11} = \frac{1}{\omega^2 \times 7.04 \times 10^{-5}},$$

$$\frac{1}{\omega} = 26.5 \times 10^{-8},$$

$$T = \frac{2\pi}{\omega} = 1.66 \times 10^{-6} \text{ seconds},$$

and the wave-length

$$\lambda = vT = 500 \text{ meters}.$$

The other curves FF', GG' and HH' give the same value of the wave-length.

Another series of experiments was performed with coils of 115 turns (inductance 31×10^{-5} henries) in the mast circuits but the experiments added nothing to the results here given.

Experiments on the conditions for resonance in the directly connected system of circuits are in progress.

Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.,
July, 29, 1905.

RESISTANCE OF TUBES TO COLLAPSE.[1]

By A. P. Carman.

THE purpose of this paper is to describe some experiments made on collapsing small brass tubes by hydrostatic pressure, and to compare these experimental results with the empirical and the theoretical formulæ which have been proposed for the resistance of metal tubes to collapse.

The only extended and systematic experiments which have been published on the collapse of tubes, are the experiments of Sir William Fairbairn made neary fifty years ago at the suggestion of the Royal Society and the British Association. Fairbairn's results are given in his paper in the Philosophical Transactions for 1858. The empirical formula which he deduced from his experiments has since been in general use in some form by engineers in the practical calculations of the strength of boiler flues. Fairbairn in his paper gives the diameters, lengths, thicknesses, and collapsing pressures for twenty-one thin iron tubes, and for five thicker tubes. As no two of the thicker tubes were exactly alike in construction, the formula deduced was almost wholly based on the experiments with the thin tubes. These thin tubes were made of single sheets of tinned iron plate, bent into a cylindrical shape, riveted and soldered. All were 0.043 of an inch thick. Five diameters, 4″, 6″, 8″, 10″, and 12″, were used in the experiments, and the lengths ranged between 19 inches and 60 inches. Fairbairn's empirical formula is

$$p = 806{,}300 \frac{t^{2.19}}{ld}$$

where p equals the external pressure in pounds per square inch, t equals the thickness of the walls in inches, l equals the diameter in feet, and d equals the diameter in inches.

This formula obviously holds only for limited lengths, for the collapsing pressure can not decrease indefinitely as the lengths increase. The numerical constant must also vary with the elastic properties of the material. The formulæ adopted by the British Board of Trade, Lloyd's Marine Underwriters, and the U. S. Inspectors of Steam Vessels, have no theoretical value, being merely working variations of Fairbairn's formula. Many writers have shown the insufficiency of the above formula and have studied the data and deduced new empirical formulæ. Such are the formulæ of Grashof[1] of G. H. Love[2] and W. C. Unwin.[3] Professor Unwin was an assistant in Fairbairn's experiments, and nearly thirty years later, gave a discussion of the same results, seeking to deduce a formula which should have some relation to the ordinary formulæ of applied mechanics. His formula was based on no new experiments and has not been accepted, its insufficiency having been shown by several writers.

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[1] A paper read before the American Physical Society in Chicago, April 23, 1905.

Theoretical treatment of the problem has been presented within a few years by three Cambridge mathematicians, G. H. Bryan[4] A. B. Bassett[5] and A. E. H. Love.[6] The problem is one in the stability of an elastic system, and, as Love says, is one of the most difficult in the theory of elasticity. Mr. Bassett in his paper in the Phil. Mag., for September, 1892, "On the Difficulties of Constructing a Theory of the Collapse of Boiler-Flues," attempts, however, to show that while the solution proposed by Mr. Bryan and himself is imperfect and not rigorous, yet it is probable for practical purposes a sufficient approximation. Bryan, Bassett and Love, with slightly different methods and assumptions, came to substantially the same expression for the collapsing pressure of a tube of indefinite length. Love's statement is: "No flue however long can collapse unless the pressure exceed $2E/(1-\sigma^2)\,h^3/a^3$ and that when the pressure exceeds this limit any flue will collapse, if its length exceed a certain multiple of the mean proportional between the diameter and the thickness." In the above expression, E is Young's modulus, σ is Poisson's ratio, h is half the thickness of the wall, and a is the radius of the middle surface of the tube. No experimental tests of these theoretical deductions have been published so far as we know.

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[1] Zeitschrift d. Vereins deutscher Ingenieure, vol. 3, p. 234.

[2] Todhunter and Pearson's History of Elasticity, vol. 2, p. 667.

[3] Proc. of Inst. C. E., 1876, vol. 46, p. 225.

[4] Proc. Camb. Phil. Soc., VI., 1888.

[5] Phil. Mag., vol. 34 (1892), p. 221.

[6] Theory of Elasticity, vol. II., p. 315.

The experiments described here were started to test the empirical formula of Fairbairn, particularly for fixing a limit on the length to which that formula is applicable, a point altogether omitted by Fairbairn. The experiments soon showed the narrow limits and the inadequacy of Fairbairn's formula. Attention was then drawn to the theoretical solution of the three mathematicians. The experiments were made on seamless brass tubes of small diameters. The tubes were placed in the stout steel receiver of a Cailletet apparatus, and hydrostatic pressure was produced by a Cailletet pump. It was found that the impact which came with the collapse of the tube injured the hard rubber valves of the pump, and the time required to get the valves working again after the collapse of each tube, made the experiments very tedious. So a valve was put in to cut off the pump from the receiver after a sufficient prelimi-

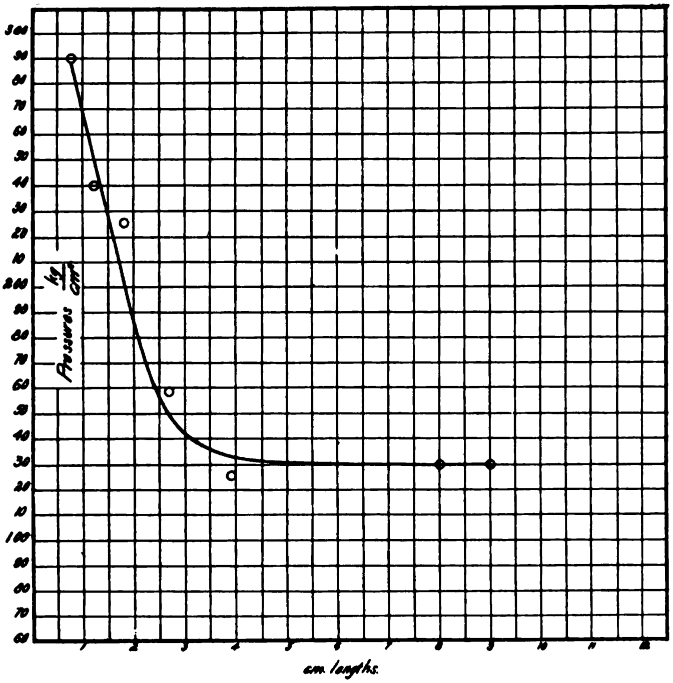

Fig. 1.

nary pressure was reached. The final pressure was then produced by a piston compressor, the piston being forced in by a screw. This auxiliary piston compressor was constructed specially for this work in the machine shop of the department. This arrangement had an added advantage that the pressure was increased gradually and the exact collapsing pressure could be more easily read. The pressures were read from a Bourdon gauge made by Shaeffer and Budenberg. The ends of the tube were closed by brass plugs soldered in, and the inside of the tube was connected with the atmosphere. The collapse came suddenly, and the hydrostatic pressure fell immediately to atmospheric pressure. As may be seen from the data given below, pressure up to 858 kilograms per square centimeter were used. The tubes in the experiments were commercial seamless brass tubes, purchased from the same jobber, with the idea of obtaining uniform material, but unfortunately the brass in the different tubes was not the same. In any one size

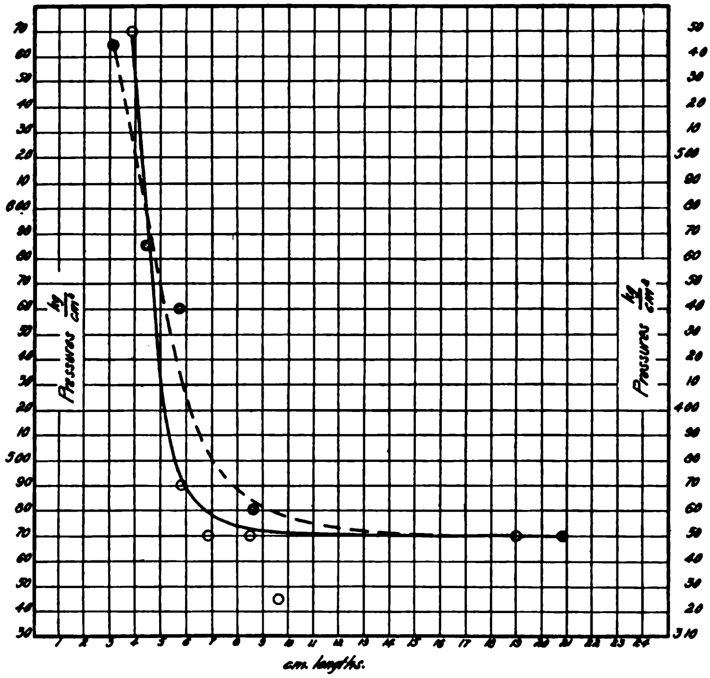

Fig. 2.

there was, however, remarkable uniformity, as shown by the tests. A considerable number of tests were made on brazed tubes purchased in the market, but there was such a variation in the results in samples from the same piece of tubing, that nothing could be made of the tests. With larger tubes this might not be found the case. The lengths, diameters, thicknesses, and the collapsing pressures are given in the following table and curves. I am indebted to Mr. F. C. Brown for many of the observations.

Table of Collapsing Pressures for Seamless Brass Tubes.

Mean Diameter.	Thickness of Wall.	Length.	Collapsing Pressure.
.891 cm.	.041 cm.	8 mm.	290 kg./cm.^{2}
"	"	12 "	240 "
"	"	18 "	225 "
"	"	27 "	158 "
"	"	39 "	125 "
"	"	80 "	130 "
"	"	90 "	130 "
"	"	39 "	670 "
1.12 cm.	.08 cm.	58 "	490 "
"	"	69 "	470 "
"	"	85 "	470 "
"	"	97 "	450 "
"	"	190 "	470 "
1.83 cm.	.08 cm.	31 "	545 "
"	"	44 "	465 "
"	"	58 "	440 "
"	"	77 "	360 "
"	"	208 "	350 "
"	"	87 "	840 "
1.78 cm.	0.135 cm.	89 "	858 "
"	"	130 "	850 "
"	"	130 "	845 "
"	"	132 "	840 "
"	"	134 "	850 "
"	"	210 "	850 "

An inspection of these data and curves, Figs. 1 and 2, shows immediately that there is a minimum length for each tube beyond which the collapsing pressure is constant, and further, that this minimum length is quite definite. Again, we see that for lengths less than this critical minimum length, the collapsing pressures rise rapidly. As definitely as can be determined from these small tubes, the collapsing pressure varies inversely as the length, for lengths less than the critical length. In this they follow Fairbairn's formula, and suggest that Fairbairn's tubes were all less than their critical lengths. An inspection of the woodcuts which Fairbairn gives for each of his experiments and comparing them with the shapes of the brass tubes which we have collapsed confirms this. Figs. 3 and 4 show shapes and sections of the collapsed tubes of the curve for Fig. 1. Fairbairn's shapes are exactly those which we have gotten for lengths less than the critical length. In the quotation made above from Love, it is stated that this minimum length is a multiple of the mean proportional between the thickness and the diameter. It is to be presumed that for the same material, this multiple should be a constant. But the data on these small tubes were not found sufficient to determine this factor of the mean proportional. The annealing of the tubes is probably not the same. In the case of one size tube upon which we have excellent data, viz., the tube with a mean diameter of 1.78 cm. and a thickness of 0.135 cm., we were fortunate in getting a value of Young's modulus for the brass. This was kindly obtained by Professor A. N. Talbot in the Laboratory of Testing Materials of the University of Illinois. Using this value, 11.5×10^{11} dynes per square centimeter (a high value for brass), and assuming corresponding value for Poisson's

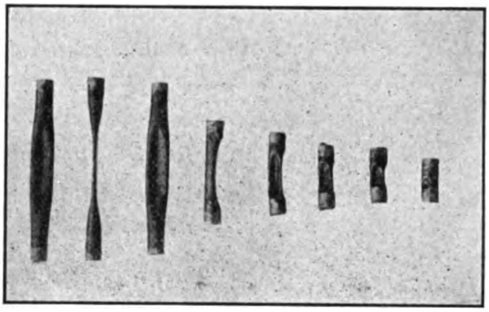

Fig. 3.

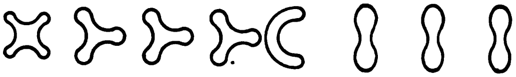

Fig. 4.

ratio, we calculated the value of the collapsing pressure from Bryan's formula, and got a value of 10.4×10^{11}. The experimental value was 8.5×10^{11}, a number of the same order, and probably as good a confirmation as could be expected from a single experiment.

These experiments on small brass tubes have shown that formulæ of the Fairbairn type are inadequate, and that for tubes of sufficient length, a formula of the type of that proposed by Bryan and Love is more nearly true. Most boiler flues used in modern boilers probably follow this formula. Arrangements are now being made to get results on large steel tubes such as are used in modern boiler construction, and it is hoped thus to eliminate the errors due to differences in annealing, etc., of small tubes, and test further the practical application of the formula.

Physical Laboratory,
University of Illinois,
April, 1905.

THE DISTILLATION OF AMALGAMS AND THE PURIFICATION OF MERCURY.

By Geo. A. Hulett and Howard D. Minchin.

IT has frequently been stated that, on distilling amalgams, metals distill over with the mercury, but the experimental evidence is not conclusive. C. Michaelis[1] found that electrical conductivity offers a very delicate means of detecting a trace of a metal in mercury. He found no impurity in the distillates from amalgams distilled in a mercury pump vacuum, but when the amalgams were distilled in a partial vacuum of (26 mm.) impurities were detected in the distillates, however in the latter case it is mentioned that there was much bumping. Victor Meyer[2] tested this question by distilling mercury, containing Bi, Pb, Sn, Cu, etc., from porcelain retorts at atmospheric pressure. The distillates were tested analytically and found to contain impurities. Only after the twelfth distillation did the distillate give a negative test for other metals than mercury, but in this work also there is no assurance that some of the amalgam did not spurt over during the distillation, as there is much bumping unless mercury is distilled in a Torricellian vacuum.

The well known method of preventing bumping by allowing a gas or vapor to bubble up through the liquid in the still will also effectively prevent the bumping of mercury. Mercury may therefore be distilled under diminished pressure and with very simple apparatus as proposed by one of us.[3] At that time mercury and amalgams were distilled in an aspirator vacuum of 20 mm. pressure, with air bubbling up through the mercury from a fine capillary, as described in the second part of this paper. With this method there is no suggestion of bumping, and although the distillation proceeds very rapidly there is very little ebullition. It is certain that nothing but vapors are carried over to the condensing tube. Zinc and cadmium amalgams were distilled and the distillation carried to completion, but neither zinc nor cadmium were detected in the distillate, and the method used, electromotive force, would detect one part of zinc in ten million to one hundred million parts of mercury. These metals undoubtedly have at this temperature a vapor pressure, for when amalgams are used in the mercury vapor lamp the metals appear prominently in the vapor. Recently Krafft[1] has shown that cadmium begins to volatilize at 156°, in a vacuum and in time deposits a mirror on the colder parts of the tube. Zinc exhibits the same phenomenon at 184°.

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[1] C. Michaelis, Inaug. Diss., Berlin, 1884.

[2] Victor Meyer, Berichte, 1887, p. 498.

[3] Geo. A. Hulett, Zeitschr. Phys. Chem., 33, 611, 1900.

We have repeated the experiments recorded in the paper mentioned above, and with the same negative results even though the electromotive force method of detecting zinc in mercury has been refined so that we can now detect one part of zinc in ten billion parts of mercury. Calculation shows that such an amalgam in the form of a vapor at 20 mm. total pressure would have a partial pressure of zinc of only 6×10^{-8} mm., but in view of the work of Krafft, l. c., zinc at 200° must have a greater pressure than this. It seems probable that zinc volatilizes with the mercury, but in our form of still it is oxidized by the oxygen of the air which is continuously bubbled through to prevent the bumping. We have frequently noticed that the distillate is not always bright when distilled from a concentrated amalgam,[2] but when it is filtered through a pin hole the mercury is perfectly bright and shows not a trace of zinc, that is, it shows less than one part in ten billion parts of mercury.

The probability that the air bubbling through the mercury in the still not only prevents bumping, but also plays the very prominent rôle of oxidizing less noble metals that may get into the mercury vapor, is of considerable importance in the purification of mercury. To test this a Weinhold[3] mercury still was constructed and zinc amalgam distilled in it. The mercury hardly boiled and there was not a suggestion of spurting but we readily detected zinc in the distillate even when there was only one part of zinc to one thousand parts of mercury in the still. In the Weinhold still the distillate forms a continuous mercury pump and the mercury vapor in time removes every trace of air. Our still was charged with pure mercury and the distillation carried on about 5 hours to remove all the air, then zinc amalgam, one part by weight of zinc to one thousand of mercury, was introduced into the reservoir, and was finally brought into the still by elevating the reservoir. There was a known amount of mercury in the tube leading from the reservoir to the still, and this mixed with the amalgam and diluted it so that the concentration of zinc was reduced to 1 part of zinc to 1,160 parts of mercury. This amalgam was distilled and the very first distillate showed 1 part of zinc to 10^8 parts of mercury. As the distillation proceeded, the concentration of the zinc in the amalgam increased until finally zinc began to separate and appear at the edge of the boiling amalgam and on the sides of the still above the amalgam. During the distillation separate portions of the distillate were removed and saved for further examination. The samples Nos. 27, 28, and 29, were removed after zinc had separated from the amalgam, and we may assume that the vapor which condensed to form these samples was saturated with zinc vapor. This conclusion seems justified as there was considerable solid zinc in the still and there was no suggestion of an oxide or coating on either the zinc or amalgam. These samples, Nos. 27, 28 and 29, were tested for zinc, as will be described below, and showed 1 part of zinc to 10^6 parts of mercury. We know also the pressure in the still (20 mm.) and from this data we may calculate the partial pressure of the zinc vapor in the still. According to Ostwald (Lehrbuch d. allg. Chem., I., 642), we have $Q_1 : Q_2 :: P_1D_1 : P_2D_2$ where Q_1 and Q_2 are the relative amounts of zinc and mercury in the distillate. P_1 is the desired pressure of the zinc and D_1 the vapor density of zinc (65), P_2 is the partial pressure of mercury (20 mm.) and D_2 its vapor density (200). Taking $1 : 10^6$ as the ratio of zinc to mercury in the distillate we have:

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[1] F. Krafft, Berichte der Deutsch. Chem. Gesell., 38, 255, 1905.

[2] Geo. A. Hulett, Zeitsch. Phys. Chem., 33, 611, 1900.

[3] Carls. Rep., 9, 68. The Weinhold still has been many times modified and improved, *e. g.*, Clark, Phil. Mag., 17, 24; Dunstan and Raymond, Phil. Mag., 19, 367; Smith, Phil. Mag., 29, 501; Nebel, Carls. Rep., 23, 236; Morse, Amer. Chem. Journ., 7, 60.

$$1 : 10^6 :: P_1 \times 65 : 20 \times 200,$$

from which $P_1 = 0.00006$ mm. This pressure of 0.00006 mm. is the calculated vapor pressure of zinc some 220° below its melting point (419°), for the temperature in the still was about 200°. Although no great accuracy can be claimed for this result, nevertheless it is interesting as giving an idea of the vapor pressure of a metal in the solid state. The above results show that not only zinc but also zinc amalgam gives a measurable vapor pressure of zinc at 200°, and further that the Weinhold still does not completely remove zinc from mercury.

THE METHOD OF DETECTING A TRACE OF ZINC IN MERCURY.

A trace of zinc has an extraordinary effect on the electromotive force of a mercury electrode. This fact is the basis of the method developed for testing the distillates mentioned above. In the previous work the combination Hg | H_2O CO_2HgO | Zn was used and saturated with CO_2 at 25°, gave an e.m.f. of 1.445 volts. This cell was very constant and on replacing the mercury by an amalgam containing only 1 part of zinc to 10^7 or 10^8 parts of mercury, a slightly lower e.m.f. was noticed. We have tested a number of combinations and find two which give some quantitative knowledge of the amalgams. The combination, Zn-amalgam | $ZnSO_4$ (saturated solution) | Zn-amalgam, allows us to calculate the concentration of one amalgam if we know that of the other and determine the e.m.f. Richards and Lewis (Zeitsch. f. Phys. Chem., 28, 1, 1899), have shown that the theoretical and observed values for zinc and cadmium amalgams of moderate concentration are in very good agreement. For dilute amalgams we find the following values:

			Observed.	Calculated.
1 : 10^3 Zn-amalgam	$ZnSO_4$	1 : 10^4 Zn-amalgam	0.02920 volts	0.02924 volts
1 : 10^4 Zn-amalgam	$ZnSO_4$	1 : 10^5 Zn-amalgam	0.04366	0.02924
1 : 10^5 Zn-amalgam	$ZnSO_4$	1 : 10^6 Zn-amalgam	1.1430	0.02924

The measurements were made at 25° and the calculated values obtained from the well known equation

$$\pi = \frac{RT}{ne} ln \frac{C_1}{C_2}.$$

These interesting deviations will receive further attention, but for our purpose the combination serves to give an idea of the concentration of zinc up to 1 : 10^6. The samples of the distillate from the

Weinhold still were now examined by comparing them with a 1 : 10^5 amalgam in an *H* cell with a saturated zinc sulphate solution as electrolyte. All of the samples up to no. 26 were cathode against a 1 : 10^5 amalgam, giving a e.m.f. of from 1.15 to 1.17 volts. It will be seen that this indicates a greater dilution than 1 : 10^6. In testing the samples which were collected after zinc separated in the still, nos. 27, 28 and 29, it was found that no. 27 and 29 gave 1.140 and 1.44 volts respectively when compared with the 1 : 10^5 amalgam showing a Zn-amalgam of almost exactly 1 : 10^6. The sample no. 28 contained so much more zinc than any other sample (1 part to 5,000 parts of mereury), that it was disregarded in calculating the vapor pressure of zinc.

In testing the very dilute amalgams a method was used in which they were compared with pure mercury. The electrolyte chosen was that of the calomel electrode (a molecular solution of potassium chloride saturated with mercurous chloride). This combination, dilute Zn-amalgam | KCl.HgCl | mercury, was first tried in the *H*-cell used above, but there were so many disturbances that it was quite impossible to get constant readings. It seemed probable that the difficulty was due to changes in the thin layer of electrolyte which creeps down between the glass and electrode. The area of this layer is large and if changes occurred it would be slow to come to equilibrium with the main portion of the electrolyte. The following form of cell was devised to obviate this difficulty.

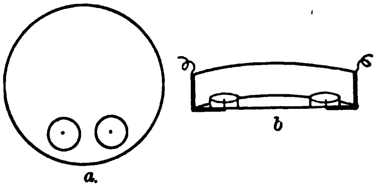


Fig. 1.

Fig. 1 represents a crystallizing dish in which are two little mounds of paraffine 5 mm. high and 25 mm. across and with very slightly concave tops. Two platinum contact wires were passed through little holes in the bottom of the dish and extended up 1 mm. through the paraffin. The bottom of this dish was covered with mercury which surrounded the paraffin mounds and gave them the appearance of two little islands. The clear electrolyte (it is important that all solid mercurous chloride be excluded) was poured over all, and it was mechanically stirred to insure its being in equilibrium with mercury. If the platinum wires were clean they showed no e.m.f. and the cell was ready to receive the electrodes. Experience showed that it was best to introduce the electrodes (mercury or amalgam) with little glass ladles which enabled us to bring the mercury or amalgam onto the little islands in the form of single globules. This point was important, as other methods of introducing the electrodes produced many little globules, and when these globules united to form larger ones marked changes in the e.m.f. appeared. The little ladles were made by cutting off the bottom of test-tubes and fusing on glass handles. To avoid the coating that collects on amalgams, the sample was drawn up into little pipettes and about 1 c.c. run into the ladle. The sample was clean and bright and could be brought onto one of the islands in the form of a single globule which was some 25 mm. across and presented a relative large surface to the electrolyte. Preliminary tests were made with pure mercury (our pure mercury was purified in the wet way and then distilled five times in the still described below). Two globules of this mercury were simultaneously placed on the little islands. The galvanometer was unsteady, showing a slight e.m.f. first in one direction and then in the other, but after half an hour, or less if the solution was stirred, the galvanometer came to rest at zero. When we now removed one of the globules and introduced another of the same pure mercury a decided e.m.f. was observed. The globule last introduced became cathode by 0.00070 volt and increased to a maximum of 0.00280 volt, and then, in about half an hour, the e.m.f. disappeared. Evidently it takes some time for mercury to come to equilibrium with an electrolyte; perhaps the Helmholtz double layer does not form as rapidly as supposed. These results showed that it was necessary, for our purpose, to introduce the mercury and the amalgam simultaneously, and measure the e.m.f. at intervals for half an hour. In this manner the cell was tested with amalgams of known concentrations. An amalgam containing 1 part of zinc to 10^8 parts of mercury showed a maximum of 0.00077 volt against pure mercury. The $1:10^9$ amalgam showed 0.00037 volt, and a $1:10^{10}$ zinc amalgam showed 0.00010 volt. This value for the $1:10^{10}$ amalgam was somewhat uncertain, but the behavior was distinctly different from that of pure mercury. One can with certainty detect one part of zinc in ten billion parts of mercury and it is undoubtedly the most delicate method known for detecting a trace of one substance in another.

With this cell we tested the samples of the distillate collected from the Weinholdt still. The purest contained 1 part of zinc to 10^8 parts of mercury, and most of the samples up to no. 26 were $1 : 10^7$ amalgams. This is in good agreement with the results of the first method of testing these samples. Certain it is that as soon as zinc was introduced into the Weinholdt still it at once appeared in the vapor and in the distillate. Zinc amalgam was now distilled under diminished pressure and with air bubbling up through the amalgam in the still, as described below. The distillation was carried on until zinc had separated from the boiling amalgam. The last portions of the distillate were dirty looking, due to a slight coat of oxide of zinc, but when filtered through a pin-hole the mercury was perfectly bright and behaved the same as our test mercury, that is, it must have contained less than 1 part of zinc to 10^{10} parts of mercury.

The foregoing experiments show that zinc readily distills over with mercury and we can safely assume that what is true of zinc is also true of cadmium, lead, tin, bismuth, and probably of copper. Krafft, l. c., has shown that in a vacuum zinc begins to volatilize at 184° to such an extent as to deposit a decided mirror on the colder parts of the chamber. For cadmium this phenomenon was observed at 156°, for lead at 335°, for bismuth at 268°. We cannot expect to completely remove these volatile metals by distilling, either in a vacuum still or under atmospheric pressure, where the air is soon completely replaced by the vapor, but if air is passed through with the vapor, these metals are oxidized and thus completely removed. It seems that this is accomplished in the method of distilling mercury proposed by Hulett, l. c. Air was slowly bubbled up through the boiling mercury to prevent bumping, and now it seems that the oxygen of this air plays the further important rôle of oxidizing the metals that get into the vapor.

The still is comparatively simple and can be constructed from apparatus to be had in any laboratory. Experience has suggested several modifications of the still proposed in 1900, and we will add a detailed description. A good distilling flask with round bottom and long neck is chosen and a tube (*A*), Fig. 2, 10 mm. diameter and about 10 cm. long is sealed onto the neck above the side tube. Through this tube (*A*) fits the tube (*B*), which is drawn to a capillary that extends down to the bottom of the distilling flask, and on the upper end of this tube is fitted a piece of rubber tubing and a pinch cock (*F*) to regulate the rate at which the air bubbles up through the mercury. The joint between (*A*) and (*B*) is made air-tight by a rubber tube that slips tightly over both tubes. All this part is above the asbestos mantle (*DD′*) and never gets even warm. The flask is placed in a sand bath (*C*) and is surrounded by an asbestos mantle (*DD′*), and this asbestos mantle is covered by pieces of asbestos. The delivery tube is cut off just outside the mantle and a thin-walled tube (*E*), 2 cm. in diameter and about 50 cm. long is sealed on, an operation that can be readily performed with a dentist's hand blowpipe. We have found that a condensing tube of the above dimensions is most effective and allows a very rapid distillation. The condensing tube ends in a narrow tube that bends down and passes

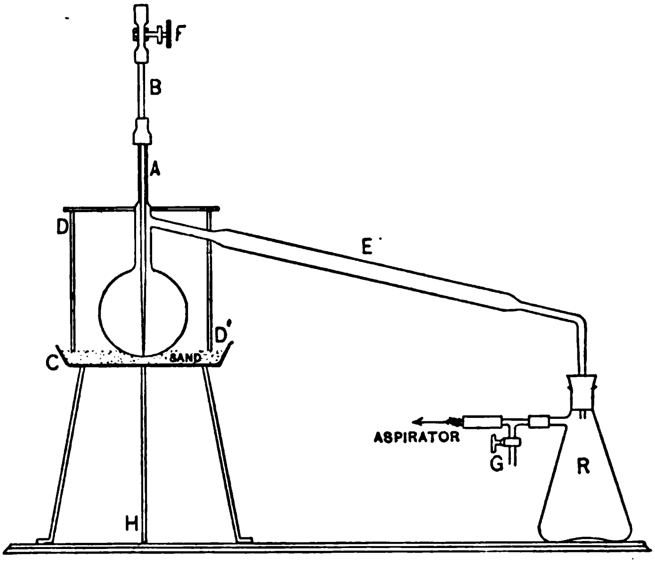


Fig. 2.

through a cork into a receiving bottle or flask (*R*). Through a second hole in this cork passes a tube which is joined by a rubber tube to an aspirator. It is best to use a common cork and make it air-tight with sealing wax. If a rubber cork is used and the distillation becomes too rapid, the vapor may condense in the tube passing through the cork, melt the rubber and produce unpleasant results. In the tube leading to the aspirator is inserted a T-tube and cock (*G*) that serves to relieve the vacuum in the system when it is desired to diminish the rate of distilling on starting the still. The still is charged, the tube (*B*) adjusted and the bunsen burner (*H*) is lighted. The aspirator is then started and the screw pinch cock (*F*) is adjusted so that air bubbles through the mercury at the rate of one or two bubbles a second. The rate of distillation is liable to be very rapid at first, due to superheating, but it can be readily checked, if the pressure is increased in the system, by admitting a little air through the cock (*G*). The flame is regulated until the rate of the distillation becomes steady and the condensation is taking place along the greater part of the tube (*E*). If the burner gas pressure is constant and the aspirator maintains a constant vacuum, the still will need no further attention and the distillation may proceed to completion. One may distill several kilograms and in a much shorter time than with the Weinhold still and distill it completely, or a very small amount may be distilled. The temperature, with a 20 mm. vacuum, is about 200°. To furnish the heat one could construct an electric furnace that would keep a very uniform temperature. One may distill at atmospheric pressure and force air through the tube (*B*), but then the temperature required would be 360°.

Instead of a flask for collecting the distillate one may seal on a long delivery tube, extending down from the end of the condensing tube (*E*) some 80 cm., and then bending up again (Fig. 3). This improvement, suggested by Minchin, avoids the use of a cork. The aspirator connection may be made at the lower end of the condensing tube (*E*), or from the neck of the distilling flask by sealing a side tube onto the tube (*A*). This makes the apparatus more fragile, but the joints can be readily made if the hand blowpipe, mentioned above, is used.

It is a comparatively easy matter to distill mercury and obtain it in an exceedingly high degree of purity. The metals that are not readily oxidized: silver, gold and platinum, have high melting points and probably require corresponding high temperatures to volatilize them, while oxidizable metals need not be feared if distilled as above.

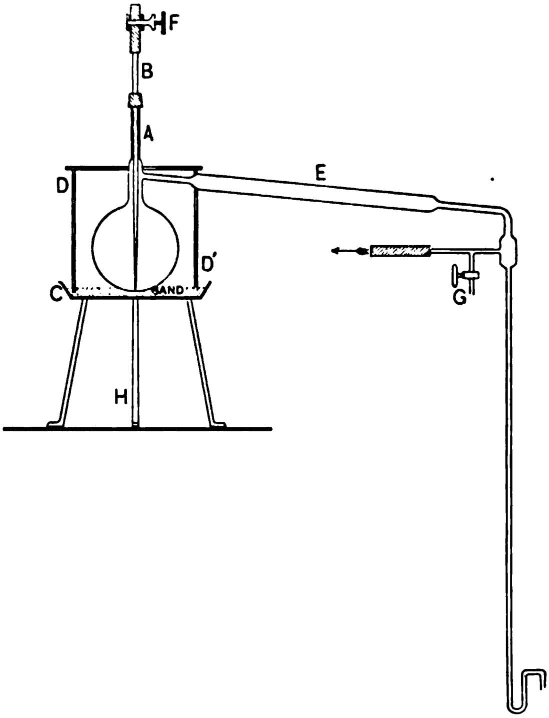


Fig. 3.

To purify mercury in the wet way it is best shaken in a separatory funnel with a molecular solution of mercurous nitrate in nitric acid. Shake for about one half hour, then run into another separatory funnel containing distilled water, and finally through a pin hole in a filter paper. This does not remove metals completely, but gives a very pure product.

We have tested the well known method of V. Meyer, *i. e.*, letting mercury fall in a fine stream through a meter column of nitric acid. A 1:1,000 zinc amalgam was thus treated, but it still contained much zinc; and even after being passed through seven times, zinc was detectable. Most other metals have a less solution pressure than zinc, so, for their removal, this method is even less favorable.

An excess of Hg_2SO_4 in sulphuric acid 1:10 forms a good solution for removing impurities if shaken with the mercury for a sufficient time. It is best to employ a mechanical shaker or stirrer and allow it to run over night.

PHYSICAL CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN, AND
PHYSICAL LABORATORY, UNIVERSITY OF ROCHESTER,
August, 1905.

USE OF A MAGNETIC FIELD WITH THE RYAN KATHODE RAY OSCILLOGRAPH.

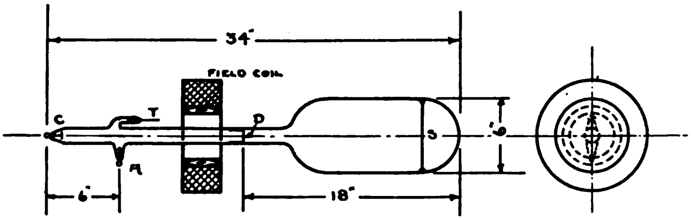
By R. Rankin.

THE effect of a magnetic field with lines parallel to the direction of discharge, upon a Crookes tube, is to reduce the terminal voltage required to maintain the discharge. This fact has been noted and studied by Birkeland, Almy and others.[1]

The writer has recently applied this principle to improve the operation of the Ryan-Braun tube, as used for the tracing of alternating current wave forms. During this work, records of the phenomena observed were taken, which, as in part confirming the results of the above named physicists may not be without interest.

The tube used in the investigations is constructed wholly of glass and is of the form shown in Fig. 1. *C* is the kathode, a flat aluminum disk, and *A* the anode, a more or less irregular lump of the the same metal. *D* is an aluminum diaphragm closely fitting the cylindrical wall of the tube and having at its center a tiny hole through which the rays may pass on their way to the screen *S*. The latter is of transparent mica treated with a calcium sulphide coating which fluoresces powerfully when struck by the rays, thus showing a clearly defined spot upon its surface. Since the kathode rays are deflected by a magnetic field, without measureable inertia,

Fig. 1.



Ryan-Braun Tube, Showing Position of Field Coil.

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[1] Almy, Camb. Phil. Proc., Vol. 11, p. 182; Birkeland, Comptes Rendus, First Semester, 1898, p. 586.

it is only necessary to mount a set of coils carrying alternating current at a point just beyond *D*, in order to obtain on the screen a graphical representation of the wave form.

In the practical application of the above method as developed by Professor H. J. Ryan, a serious difficulty arose from the fact that, with extended use, the tube vacuum and consequently the necessary operating voltage increased rapidly, causing leakage from terminal to terminal outside the tube, and as a result, a flickering and unsteady spot on the screen. This action is mentioned in Professor Ryan's paper to the American Institute of Electrical Engineers of July 2, 1903.

Several means for reducing the vacuum have been tried, and the tube shown in Fig. 1 is equipped with the most successful of these. This consists of a platinum tube of about a millimeter diameter, cemented into the side of the glass wall and projecting in both directions from it. The outer end of this tube is closed, but the inner end is open, so that we have in reality a tiny platinum chamber connected with the kathode tube. When heated to a dull redness the platinum permits a very small quantity of gas to pass and thus reduces the vacuum and the corresponding tube voltage. The process is simple and very effective, the vacuum being reduced in a few seconds to any desired value. It may be here noted, however, that if the reduction goes below the point necessary for the production of kathode rays, no amount of passage of current through the tube will restore the vacuum. It will be seen at a glance that, since the velocity of the rays is very much greater for higher vacua, anything which tends to decrease this vacuum tends to diminish the intensity of the indicating spot, although, as previously noted, it improves the steadiness.

It had been noted during the operation of the tube that if a deflecting force in the neighborhood of the diaphragm prevented any of the rays from passing the latter, by causing them all to impinge against the metal or the glass wall, an immediate rise in voltage across the terminals of the exciting Wimshurst machine followed. This is contrary to the results found by Willows,[1] who states that below the gas pressure corresponding to minimum volts for a given tube, a transverse field causes a reduction in the terminal voltage. Willows' results were obtained by applying a magnetic field at the kathode, and he attributed the voltage drop to an alteration in the form of discharge caused thereby.

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[1] Willows, Phil. Mag., March, 1905.

In the present case, however, the voltage rise was caused by a deflection far removed from the kathode, the deflecting agent being a small horseshoe magnet which did not in any way alter the form of discharge. It is a significant fact that the same magnet acting on the rays which had just passed the diaphragm produced no effect upon the voltage.

Birkeland[1] and Almy,[2] working with magnetic fields parallel to the direction of discharge, obtained by this method considerable reduction in the voltage required to establish kathode rays in a tube of given vacuum. Each attributed the result to an alteration in the form of discharge which permitted current to pass more easily.

It is the intention of the writer to show that in some forms of tube a counter E.M.F. may exist, whose removal can be effected by magnetic lines which apparently do not alter the form or amount of discharge.

The first experiment was similar to that of Birkeland, who, however, used a straight cylindrical form of tube and developed the magnetic field by means of a powerful coil placed just outside the kathode, with its axis parallel to the kathode rays. In this

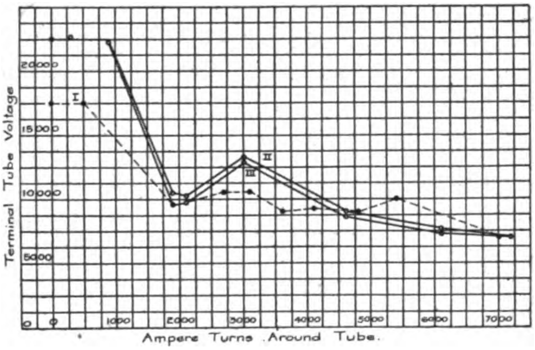

Fig. 2.

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[1] Birkeland, l. c.

[2] Almy, l. c.

manner, with the proper value of field, he was able to reduce the voltage to one tenth of its normal value. In the present case, however, the coil was placed over the tube at the point shown in Fig. 1. The dimensions of the coil were as follows:

Size of wire	No. 10 B. & S.
Length mean turn	23.6 in.
Number of turns	200
Length of coil	3 in.
Inside diameter of winding	6.5 in.
Outside diameter of winding	9 in.

Experiment 1 was conducted to determine whether the voltage drop followed any regular law; *e. g.*, whether the effect was directly proportional to the strength of the magnetic field.

The tube was excited from a motor-driven Holtz machine. A Kelvin 35,000-volt voltmeter was connected across the tube terminals, the kathode being grounded. The current in the tube was measured by a Weston milli-voltmeter, with a maximum scale deflection corresponding to about .35 milli-ampere. It was found necessary at times to use a shunt with this instrument. The current in the axial coil was measured with a Weston ammeter.

As the current in the coil was varied, the size of the recording spot underwent a continual change, at one time appearing as a circle of one or two millimeters diameter and an instant later covering the entire screen (12 cm. dia.). With the variations of field, also appeared light and dark spots which travelled along the walls of the tube, exactly as though the kathode rays were being focused, causing the formation of nodes and loops. The position of the spot for a given field was steady and its appearance more intense than under normal conditions. At very strong fields no rays impinged upon the glass walls between kathode and diaphragm. The discharge could be plainly seen proceeding down the center of the tube in a tiny bluish bundle. This bundle, however, exhibited all the characteristics of the kathode rays, *i. e.*, it produced the usual phosphorescence upon the screen, and, upon being deflected by a transverse field on either side of the diaphragm it produced the characteristic greenish patch on the glass walls. It is to be especially noted that such deflection between kathode and diaphragm, near the latter, produced a rise of voltage, while deflection between diaphragm and screen had no such effect.

In plotting the curve of voltage drop for a parallel field the axial coil was placed two inches from the diaphragm toward the kathode. Readings were made of terminal tube voltage and current for various field strengths as expressed in ampere turns on the fixed coil. The results of this run are shown in curve I., Fig. 2. It will be noticed that the normal tube voltage was 17,500. The tube current remained practically constant throughout the wide range of voltages obtained.

In order to check these results, the experiment was repeated, using the same apparatus. In the second case, however, the initial tube voltage was at the higher value of 24,000 volts. A reversing switch was placed in circuit with the magnetizing coil and readings with field direct and reversed taken at each value of ampere turns. These curves are marked II. and III. in Fig. 2. When taken in connection with the observed phenomena the results of these two runs are in close agreement.

The normal tube voltage of curve I. is 17,500. This remained sensibly constant up to about 500 ampere turns, when it dropped off very suddenly, reaching the value of 10,000 at 1,000 ampere turns and continuing to drop irregularly till the very low value of 7,000 was reached.

In the case of the two latter curves, we start with a slightly higher vacuum and consequently higher velocity. The drop in voltage first occurs at about 1,000 ampere turns, a value rather higher than before, but reaches a minimum for the first slope at about the same value of ampere turns (2,000) as in the first case. Both curves then continue somewhat irregularly down to 7,000 volts, when all curves are coincident.

In so far the above results are also in agreement with those of Birkeland, who found a large voltage drop at a certain "critical field strength," which "critical field" was greater for higher vacua.

The difference which exists between the two experiments lies in the form of discharge. With the coil placed near the cathode there occurred simultaneously with the voltage drop a total disappearance of kathode rays, the discharge being accompanied by a bluish glow from kathode to anode which exhibited none of the characteristics of the kathode rays. This fact has been also noted by the writer. With the coil at the diaphragm, however, a considerable drop may be obtained without the disappearance of kathode rays. Throughout the entire range of voltage covered by the curves of Fig. 2 there was a visible spot upon the screen *S*.

A glance at the curves I., II. and III. would indicate that the drop in voltage was due to some irregular action of the magnetic field upon the conditions governing the generation of the kathode rays, which cause them to be established at a lower potential for the same tube pressure. Close observation of the behavior of the ray, however, does not confirm this, but tends to show that while the voltage drop accompanies the field the two are not directly related, the former being in reality only a secondary effect. For, the presence of a weak magnetic field produced no effect upon the voltage. It was only when the field became strong enough to markedly decrease the impingement of the rays on the walls of the tube and to direct them more nearly toward the center of the diaphragm that any drop became noticeable. In the present case at the high value of field due to 6,000 ampere turns, the tiny blue bundle of rays could be plainly seen up to the diaphragm, the voltage being about one third of its normal value. The slightest movement of the coil which caused the rays to impinge against the glass wall or to diffuse against the diaphragm caused an instant rise of voltage. A second experiment illustrates this point even more forcibly.

A tube was taken of very high vacuum which required for the establishment of kathode rays a voltage corresponding to a one-and-a-quarter-inch spark between one-inch ball points. Using the coil previously described placed just over the diaphragm and a field strength of 6,000 ampere turns, no perceptible voltage drop could be secured, while no concentration of the rays was observed. When, however, the coil was brought to its position near the diaphragm a value of 2,000 ampere turns sufficed to darken the walls of the tube in its vicinity and the voltage immediately dropped to that corresponding to a spark gap of five-eighths inch.

We may then sum up the results of the above experiments as follows :

1. A magnetic field parallel to the path of kathode rays does not alter the amount of current taken by a kathode ray tube over the wide range of voltage obtainable with such a field.

2. A large but irregular decrease in the voltage required to produce discharge in a kathode ray tube accompanies a strong magnetic field parallel to the direction of the rays.

3. The direction of the parallel field has no effect on the results.

It is the opinion of the writer that at least part of the decrease in terminal voltage with increasing field strength is not an effect of the magnetic lines upon the generation of the kathode rays but is caused as a secondary effect.

Further, that one component of the terminal voltage is in reality due to a counter electromotive force resulting from the repelling action of those negative particles which collide with the walls of the tube and the diaphragm upon those particles which leave the kathode just behind them; and that another component of the voltage is consumed in maintaining the current under given conditions of vacuum and tube length. A third component gives to the particles their velocity. Also it is believed that the decrease in terminal voltage is in part due to the removal of the counter E.M.F. by the concentration of these rays in a tiny bundle along the axis of the tube and in part due to the reduction of the velocity component.[1]

Since in several determinations of the value e/m of kathode rays, the velocity has been assumed proportional to the square root of the voltage, the above separation of the latter into components may explain one source of discrepancy which exists between the values found by this assumption and those which employ more direct measurements.

The values of e/m as determined by Kaufmann[2] and Simon[3] using the potential method are 1.86×10^7 and 1.865×10^7 respectively.

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[1] Almy has attempted to prove the non-existence of counter E.M.F. by forming the anode of a hollow cylinder which completely surrounded the kathode, a thick wire. Using a magnetic field he was able to still produce a very decisive voltage drop. It will be seen at a glance, however, that since a field parallel to the axis of the tube would be perpendicular to a large part of the rays, while a field normal to such axis would be part normal and part parallel to these rays, we have a rather complicated action which cannot be fairly compared to the present case.

[2] Kaufmann, Wied. Ann., 61, p. 544. [3] Simon, Wied. Ann., 69, p. 589.

Wiechert[1] by comparison with the velocity of light found *e/m* as 1.26×10^7 and J. J. Thompson[2] by balancing magnetic and electrostatic forces determined a value of 1.77×10^7. The latter points out two possible sources of error in Kaufmann's method:

1. That it is impossible to assume that the tube potential is the potential of the deflected rays since many of the kathode rays are known to start from a point beyond the kathode.

2. That we have no right to assume that some of the electric energy is not consumed by collision of molecules.

The above would indicate still a third objection to the potential method, namely the consumption of energy by a counter electromotive force and by the component which maintains current.

Recent experiments have indicated that the velocity of the rays at the reduced voltages due to magnetic field is higher than when generated at the same voltage under normal conditions. This point has however not been proved conclusively enough to warrant its assertion.

In the use of a magnetic coil to improve the Ryan-Braun tube as an oscillograph,[3] it has been found possible to secure good results by using a fairly low number of ampere turns placed close to the anode. In this position the coil does not affect the shape of the card on the screen, while the advantages of using it are:

1. To secure the well defined spot of a rare medium without the troublesome flickering due to high voltages.

2. To secure a more intense spot of light by the direction of more rays through the aperture in the diaphragm.

3. To obtain a means of varying between limits the velocity of the ray and therefore the sensitiveness of the oscillograph.

In conclusion the writer wishes to express his deep obligation to Professor H. J. Ryan and Professor E. Merritt, of Cornell University, for advice and assistance, without which the above work would not have been carried out.

[1] Wiechert, Weid. Ann., 69, p. 739.

[2] Thompson, Conductivity of Electricity Through Gases, p. 91.

[3] A discussion of the kathode ray oscillograph by the writer appeared in the Electric Journal for October, 1905.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE TWENTY-NINTH MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, October 28, 1905. President Barus presided.

The society adopted the following minute expressive of the great loss sustained by itself and by the world of science in the death of our Vice President, our colleague and our friend, Professor DeWitt Bristol Brace, on October 2, 1905.

It was under the shadow of this bereavement that the autumn meeting of the society was convened — a bereavement which is a personal one to nearly every member of the organization. A frequent contributor to the program, a vice president of the Society, a charter member, and the genial friend of every other member, Professor Brace will be long and keenly missed by everyone of us. For not only have our proceedings been enriched by his contributions to knowledge, but those in attendance upon our meetings have always been inspired by his devotion to pure science, by his clear grasp of the vital connection between fact and theory, and by his experimental skill.

Born at Wilson, New York, on January 5, 1859, he took his bachelor's degree at Boston University in 1881, at the same time specializing in physics at the Massachusetts Institute of Technology. In his graduate work, he had the good fortune to come under the influence of Rowland and Helmholtz, with the latter of whom he took his doctor's degree. Two years of mathematical physics with Kirchhoff were also a potent factor in his development.

His researches, covering a wide range of optical subjects, are described mainly in *Wiedemann's Annalen*, the *Philosophical Magazine*, the *Astrophysical Journal* and the *Physical Review*, during the twenty years following 1885 when his doctor's dissertation appeared in the first mentioned periodical.

se who were associated with him as students at Baltimore and Ber-
se who have worked with him as colleagues in the University at
hose students who have come under his guidance in the labora-
hose who have accepted the generous hospitality of his home,
admiration of the fine qualities of mind and the high ideals which
at once a successful teacher and an effective investigator.
ty was innate; his courtesy, never failing; his energy and
ness of purpose, a powerful stimulus to all who knew him.

owing papers were presented:

andard Cells with Electrolytic Mercurous Sulphate as Depolar-
eo. A. Hulett.

e Phenomena of Ionization in Flame Gases and Vapors."
ts.

struments and Methods Used in the Magnetic Survey of the
tic Ocean by the Carnegie Institution of Washington." L. A.

he Transmission and Reflection of Electric Waves by Screens of
and Grids." F. C. Blake and C. R. Fountain.

e Nucleation of Dust-free Air, Energized or not, Observed at
Increasing Supersaturation." Carl Barus.

e Duration of the After Glow Produced by the Electrodeless
C. C. Trowbridge.

he Decay of Phosphorescence in Sidot Blende." E. L. Nichols
Merritt.

e Conductivity of the Air due to the Sulphate of Quinine."
Gates.

e Conductivity of the Vapor from a Mercury Arc." C. D.

The Construction and Measurement of Standards of Inductance."

Preliminary Report on a New Determination of v, the Ratio of
o-magnetic and Electro-static Units." E. B. Rosa and N. E.

ncement was made that the annual meeting of the Society would
New York City, December 29–30, 1905.
ned.

ERNEST MERRITT,
Secretary.

THE PHENOMENA OF IONIZATION IN FLAME GASES AND VAPORS.[1]

BY F. L. TUFTS.

THE paper presented the results of a large number of measurements made on the relation between ionization in the ordinary gas flame, the rate of consumption of gas by the flame and the character of the flame.

The results were also given of measurements made for the purpose of determining the possibility of obtaining a saturation current through the flame and also the relative rates of production of ions in the different parts of the flame.

The last part of the paper contained the results of measurements made for the purpose of determining the conductivity imparted to the different parts of the flame by the vapor of sodium chloride and also the relation between the conductivity of the vapor and the conditions under which it was introduced into the flame.

THE TRANSMISSION AND REFLECTION OF ELECTRIC WAVES BY SCREENS OF RESONATORS AND BY GRIDS.[1]

BY F. C. BLAKE AND C. R. FOUNTAIN.

1. The source of the waves was a Righi vibrator placed horizontally in the focal line of a parabolic mirror. The detector was an iron-constantan Klemenčič receiver similarly placed. A second receiver was used as a check. Both were tuned, their length being 4.0 cm. when tuned. The principal wave-length of the radiation employed was measured by means of an interferometer and found to be 9.8 cm., the diameter of the spheres of the vibrator being 0.952 cm.

2. The reflection and transmission of screens of tin-foil resonators in air were determined, as the length of the resonators was constantly lessened. For the case where the resonators were three centimeters apart sidewise, *i. e.*, in a direction perpendicular to the electric force or to the axis of the vibrator, maximum resonance was obtained for a length 5.3 cm.

3. The same measurements were repeated for resonators on glass and the effect due to different distributions of resonators was studied. A variation in the distribution end-on, *i. e.*, parallel to the electric force, altered the percentages of transmission and reflection but did not affect the resonating-length. A variation in the distribution side-on, *i. e.*, perpendicular to the electric force changed the length for maximum

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[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905. The paper itself will appear in a later number of the PHYSICAL REVIEW.

resonance or the resonating-length. This effect proved to be an inverse one, an increase in the side-on distance between resonators, causing a decrease in the resonating-length. It was noticed that for a side-on distribution ranging from 2 to 7 cm. ($\frac{1}{4}\lambda$ to $\frac{3}{4}\lambda$, about), the glass, when covered with strips whose length was twice that for resonance, reflected less than when bare. This indicates a lessening in the index of refraction of the glass, a phenomenon that finds a possible explanation in the Ketteler-Helmholtz dispersion theory.

4. The reflection and transmission of grids (continuous strips) in air and on glass were measured and then the grids were cut into resonators and the reflection again determined. For the distribution 3 cm. side-on the reflection was for air twice, for glass ten times as great as for the uncut strips.

5. The reflection and transmission of grids of wire (B. and S. No. 34) were determined, a grid with wires 2.5 cm. reflecting 100 per cent.

6. It was estimated from data obtained in the progress of the work that the free resonator-length in air would not be far from $\frac{1}{2}\lambda$, supporting Poincaré's value of 2 for the ratio between wave-length and resonator-length, while MacDonald's value of 2.53 seems more nearly to hold for the ratio between wave-length and receiver-length.

THE DURATION OF THE AFTERGLOW PRODUCED BY THE ELECTRODELESS DISCHARGE.[1]

BY C. C. TROWBRIDGE.

THE purpose of the investigation was to study the duration of the glow that often appears after the cessation of the electrodeless discharge in gases at low pressures. Measurements made thus far on the duration of the glow in air show a maximum of duration between .15 and .02 millimeter pressure, also that this maximum point varies with the electrical conditions of the experiment. It was determined that there is a critical point between 0.7 and .3 millimeter pressure where the glow is only occasionally formed, after which as the pressure is further reduced, the duration of the glow increases rapidly to the maximum.

A study of the duration of afterglow under various conditions has shown that smooth curves can be readily obtained showing the variation of the duration of the afterglow with change of pressure of the gas. It has been found that the maximum of duration of these curves, when the electrical intensity is small, is at the same pressure approximately as the minimum sparking potential of the electrodeless discharge, or the point at which the discharge is most easily started. Also, when the frequency of the discharge is altered by a change of capacity, the position of the maximum point of the duration curve is altered to correspond to the displacement of the minimum sparking potential of the discharge.

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[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

Lengthening the spark gap and thereby increasing the electrical intensity inside of the vessel in which the discharge takes place changes the form of the duration curve, and when the electrical intensity is thus increased above a certain amount, the curve obtained is completely altered in form. The electrodeless discharge was also made to take place in a vessel at liquid air temperature and it was found that the afterglow accompanying the discharge was diminished considerably in duration and intensity at the low temperature of about —186° C. When the afterglow in the rarefied air is allowed to diffuse into a vessel cooled to liquid air temperature, the duration curve is displaced some distance towards the higher pressure and is changed in form, other conditions being the same; otherwise, the duration of the afterglow, which in the experiment was approximately thirty seconds, was found to be little different than when the air is at normal temperature. That a long-enduring glow can be obtained at the low temperature of liquid air and a pressure approximately one-tenth of one millimeter is obviously important in its bearing on problems of astrophysics.

THE DECAY OF PHOSPHORESCENCE.[1]

BY E. L. NICHOLS AND ERNEST MERRITT.

IN considering the decay of phosphorescence from the theoretical standpoint the authors have adopted in its general form the theory of luminescence proposed by E. Wiedemann and Wiedemann and Schmidt, in which it is assumed that dissociation of the active substance is produced during excitation and that the recombination of the products of this dissociation is accompanied by the emission of light. For reasons stated in a previous paper the authors think it probable that this dissociation is similiar to that produced in gases by Roentgen rays, rather than to chemical or electrolytic dissociation of the ordinary kind.

Stokes' Law is explained by the fact that the ions formed are more strongly attracted to the molecules of the solvent than were the original neutral molecules, so that recombination will usually occur when the ions are close to the solvent molecules. The vibrations set up on recombination are therefore of longer period than those natural to the free molecule of the active substance. According to this view Stokes' Law is not to be looked upon as exact, but rather as expressing a general relation between the regions of excitation and emission. An overlapping of the luminescence spectrum and the absorption spectrum, such as has frequently been observed, is to be anticipated.

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[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

The authors show that the modified theory of Wiedemann and Schmidt also accounts satisfactorily for a number of other general laws of luminescence, *e.g.*, the fact that luminescence light is unpolarized, even when excited by polarized light; and that the luminescence spectrum (in the case of a single band) is independent of the wave-length of the exciting light.

The simplest hypothesis regarding the rate of recombination of the ions in a luminescent substance is that which has been applied to the case of ionization in gases. If n is the number of positive ions present at any time t, we have

$$\frac{dn}{dt} = -an^2,$$

$$\therefore \frac{1}{n} = \frac{1}{n_0} + at,$$

and since the intensity of the phosphorescence light is proportional to the number of recombinations per second, *i. e.*, to an^2

$$I = \frac{ka}{\left(\frac{1}{n_0} + at\right)^2},$$

$$\frac{1}{\sqrt{I}} = a + bt.$$

Observations made on the phosphorescence of Sidot blende are in complete agreement with this law for 7 seconds. The constant k is a function of the wave-length of the particular region of the phosphorescence spectrum that is being studied. But the ratio a/b should be independent of k for

$$\frac{a}{b} = \frac{1}{n_0\sqrt{ka}} \cdot \frac{\sqrt{k}}{\sqrt{a}} = \frac{1}{n_0 a}.$$

Observations made at three different wave-lengths gave for a/b the three values, 1.75, 1.73 and 1.65.

The above simple law of decay does not hold throughout the whole time of phosphorescence. After ten or fifteen seconds the decay is found to be more gradual than that corresponding to the above expression for I.

The results may perhaps be looked upon as indicating a gradual decrease in the constant *a*, which change is to be anticipated on the basis of the modified dissociation theory. The long time phosphorescence of Sidot blende is now being studied.

THE CONDUCTIVITY OF THE VAPOR FROM A MERCURY ARC.[1]

BY C. D. CHILD.

AN investigation of the space in the neighborhood of a mercury arc has shown the following facts. The vapor coming from a mercury arc is highly conducting. A luminous space gradually spreads out from the arc and the front of this region has the greatest conductivity and the greatest luminosity. This conductivity is not due directly to ions coming from the arc, nor to rays sent out by it. It is not due to any leakage over the surface of the glass. It is probably not due to the high temperature of the gas.

A probable explanation is one suggested by Professor Ernest Merritt, *i. e.*, that when the ions first recombine they are in a condition of unstable equilibrium, much like the atoms of radio-active matter and that many of these combinations break up again into positive and negative ions.

There is an e.m.f. between electrodes inserted in different parts of the tube, which is possibly due to the more rapid diffusion of the negative ions.

[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

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BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

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